

POOR QUALITY

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 27X 280 281 282 28X 29X
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 332 337 338 340 342 34Y
 351 352 353 355 364 365
 366 368 36Y 373 37Y 380
 385 394 396 39Y 440 453
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 534 57X 57Y 592 593 59Y
 602 603 613 614 620 624
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 64X 658 65X 660 662 668
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 754 75X 76Y 80Y 813 BX
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 C8B4A3X C8B4G10
 C8B4G12 C8B4G14
 C8B4G15 C8B4G19
 C8B4G1 C8B4G3 C8B4G5
 C8B4G7 C8B4G9 C8B4GX
 C8B4Y D15B3D D15B4B2
 DB

(56) Documents cited
 GB 1520094
 GB 1501122
 GB 1494777
 GB 1464104
 GB 1382861
 GB 945542
 (58) Field of search
 G2C
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(54) Photographic couplers with a cleavable group, photographic materials containing them and methods of forming images

(57) Greater control on diffusibility and timing of release, etc. when using photographic couplers having cleavable photographically useful groups is obtained with novel couplers in a photographic material comprising a support, at least one photosensitive silver halide emulsion layer and associated therewith a photographic coupler comprising a coupler group and a releasable photographically useful group, characterized in that the coupler contains a timing group, joining said coupler and photographically useful groups, which is cleavable from said coupler group on reaction with oxidized colour developing agent and the resulting cleaved timing and photographically useful group entity is able to undergo an intramolecular nucleophilic displacement reaction to make available a photographically useful compound.

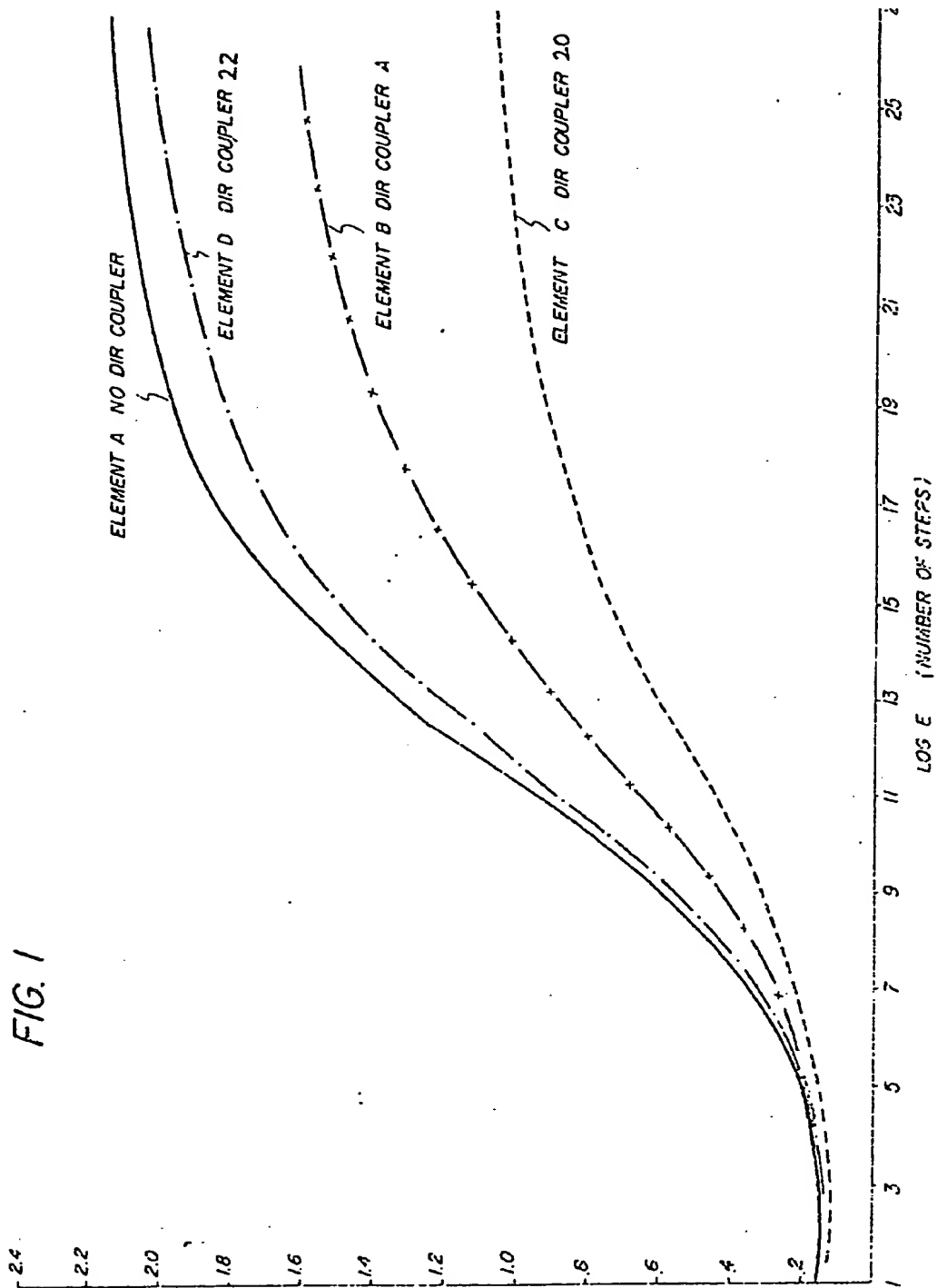
Of the specified couplers, couplers 1-22 and 36 are colour couplers which release development inhibitors, coupler 37 releases a colourless reaction product and a development inhibitor, couplers 23-29 release dyes, couplers 30-34 release competing couplers and coupler 35 releases a bleach inhibitor.

In Ex 6 there is disclosed a material containing fast and slow blue-, green- and red-sensitive silver halide layers.

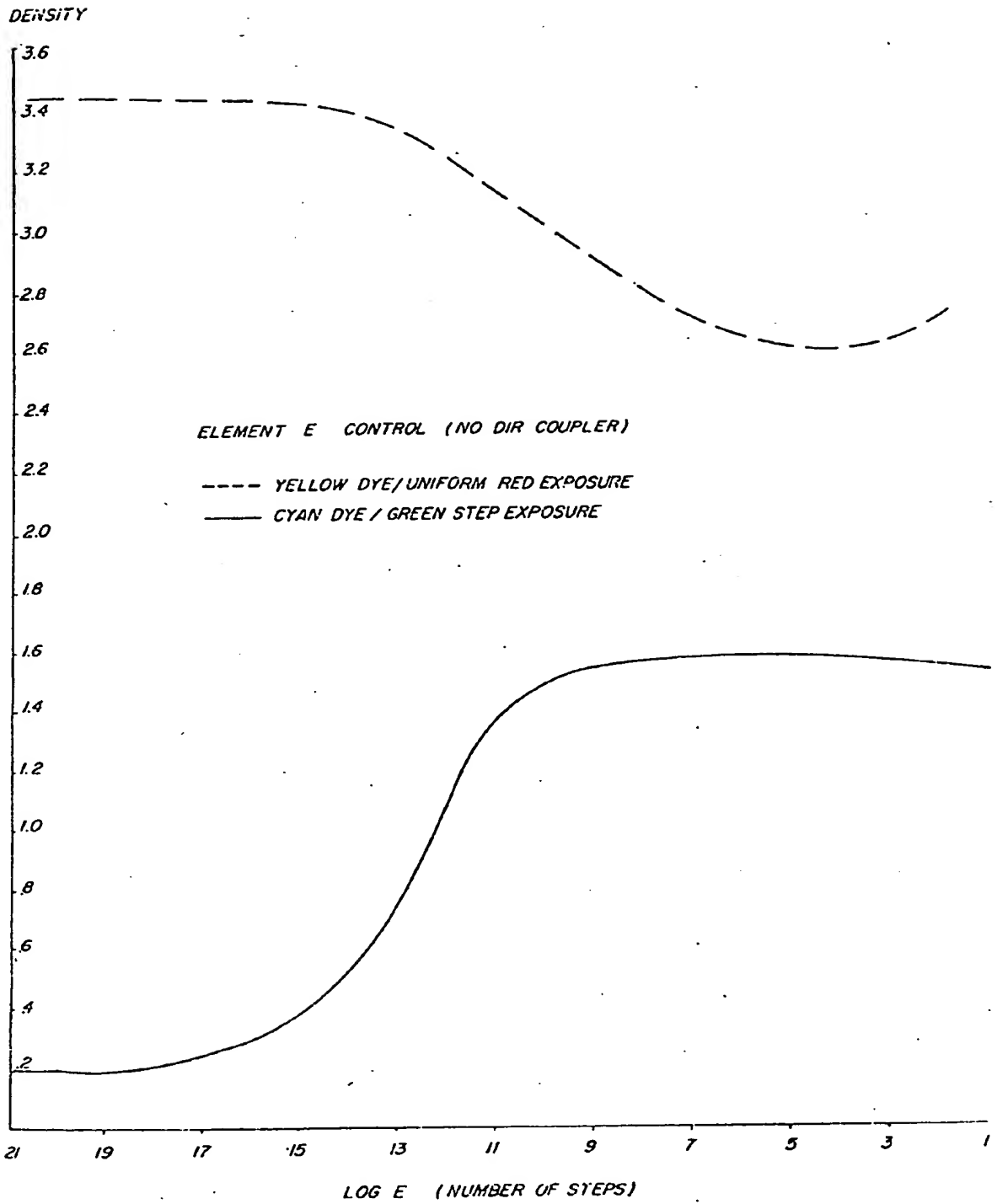
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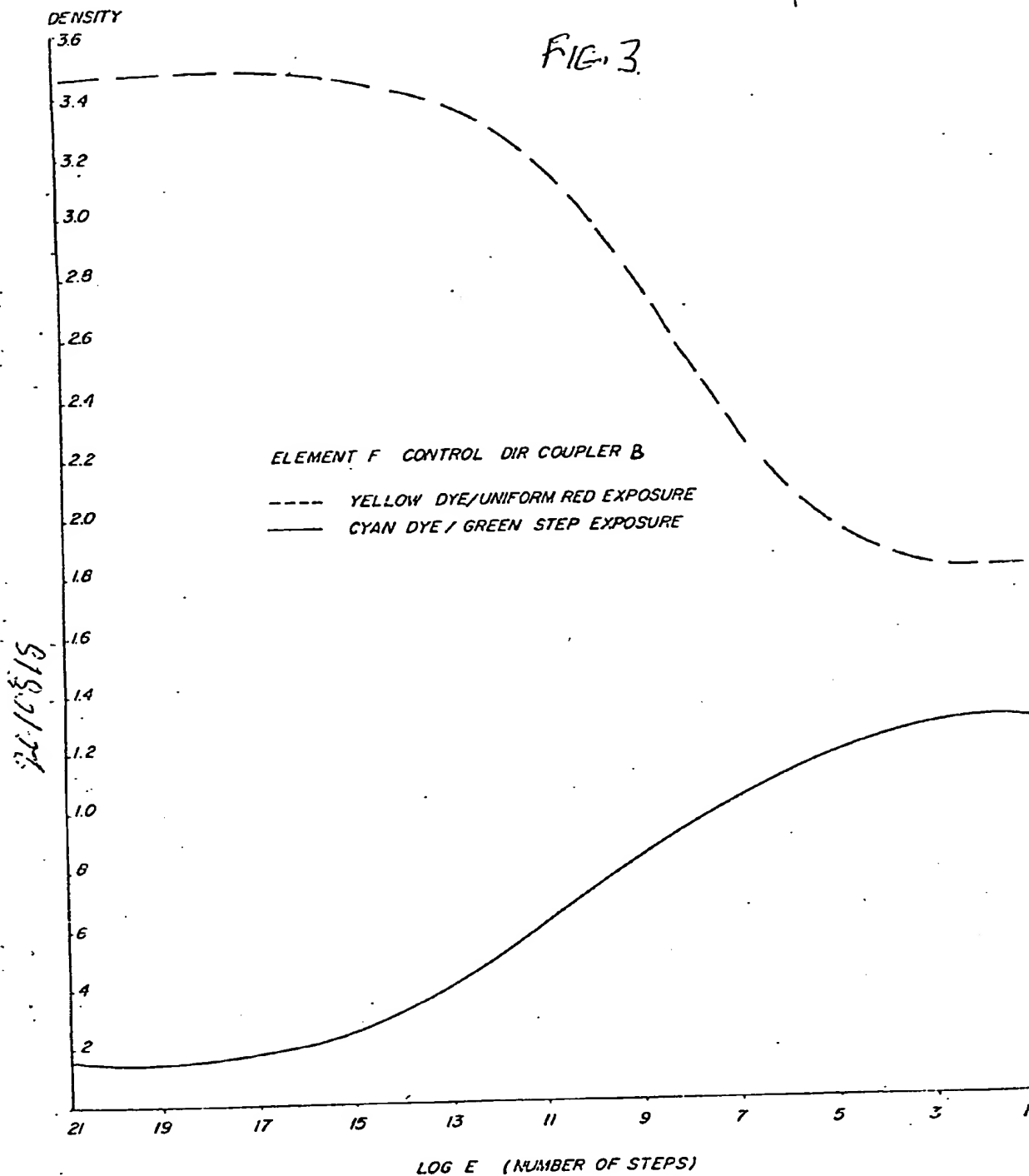
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FIG. 4

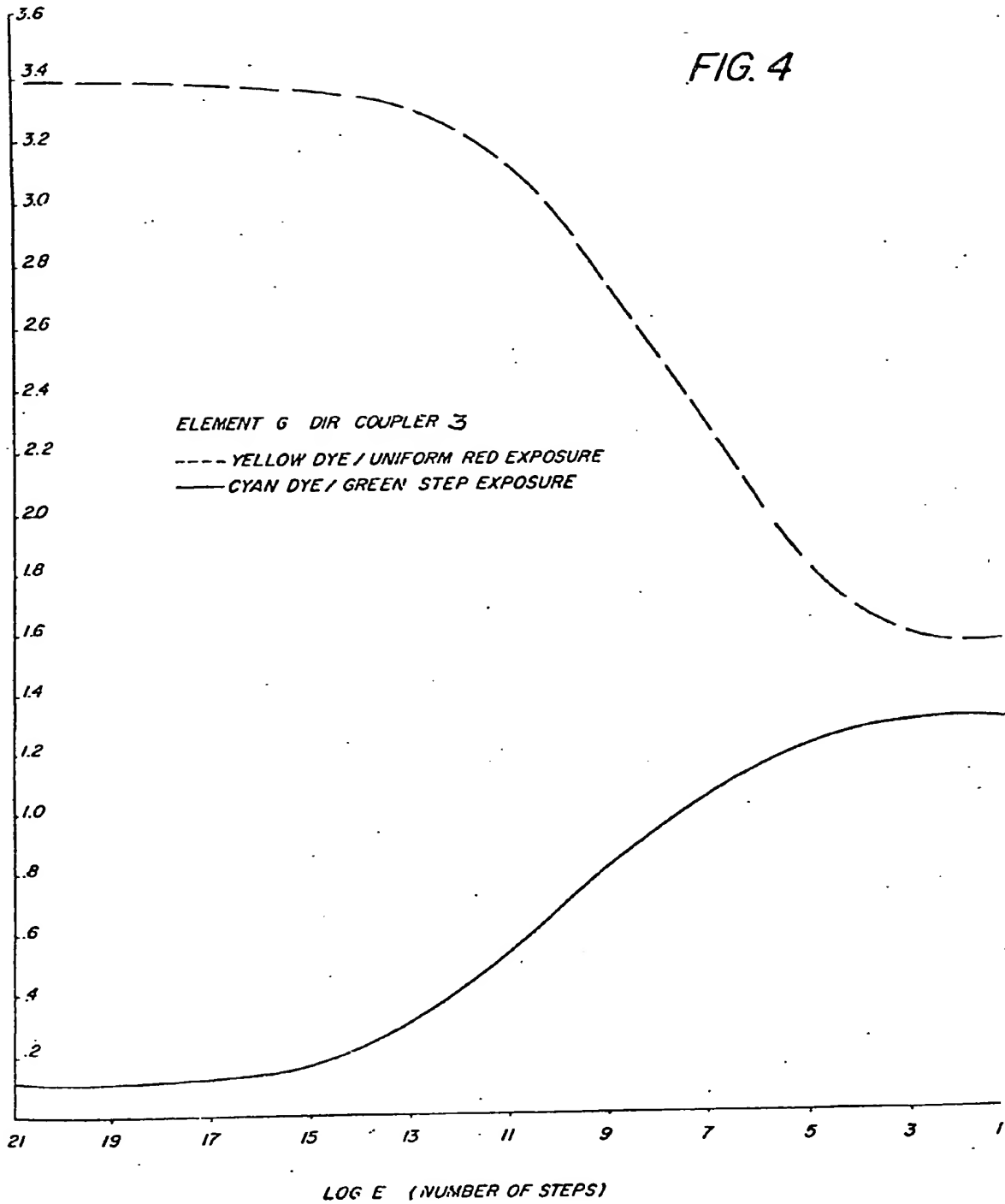


FIG 5

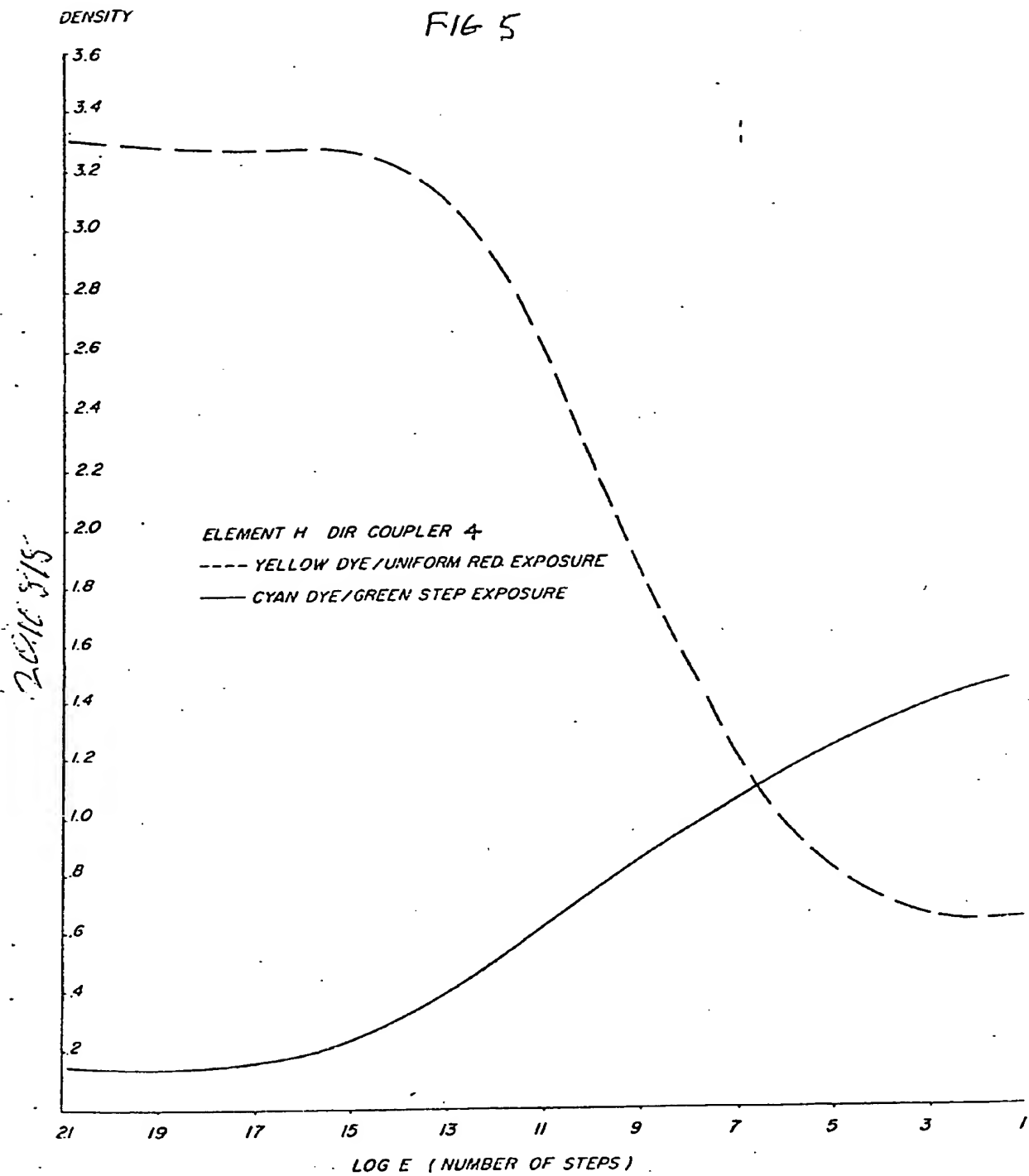
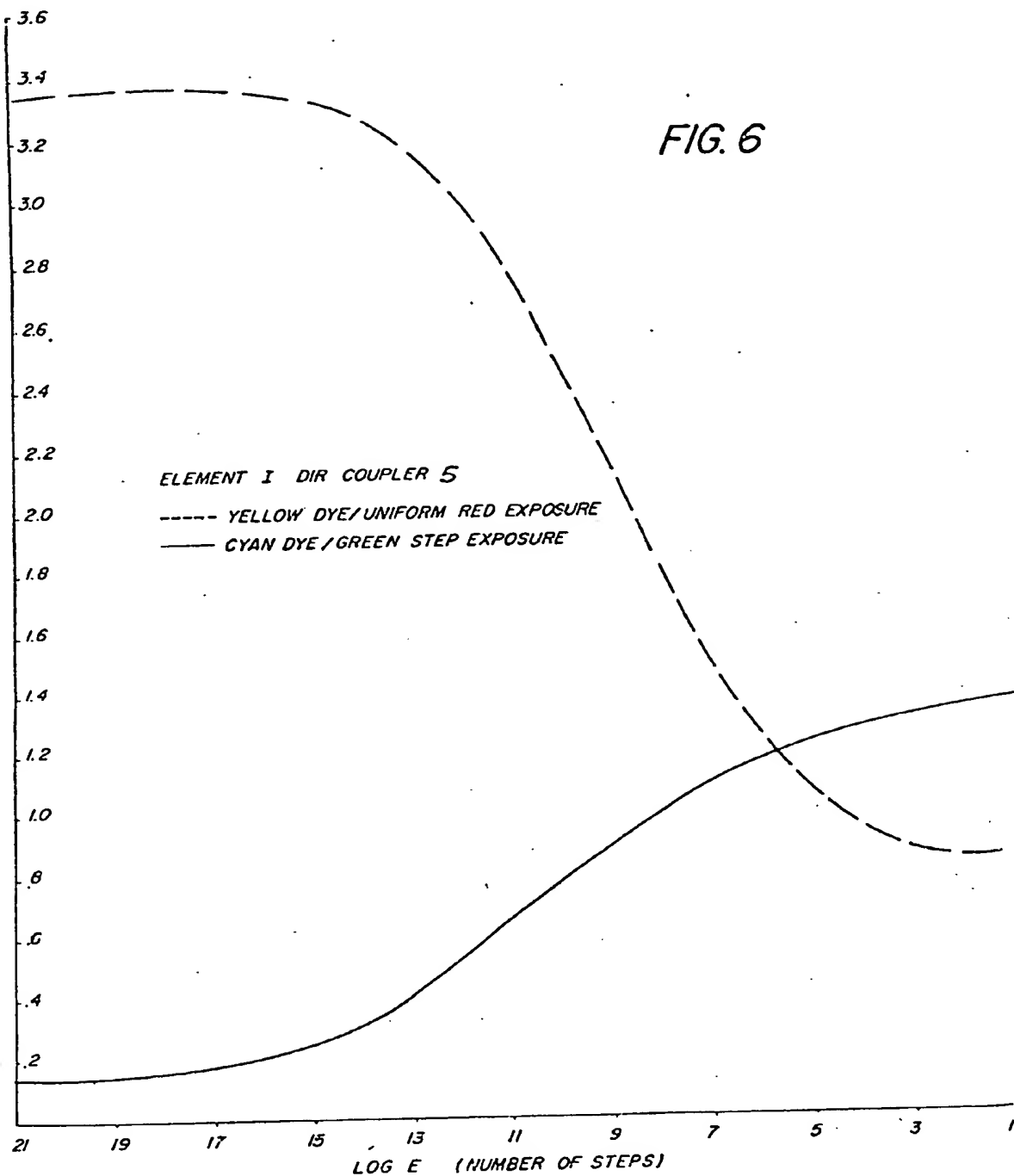
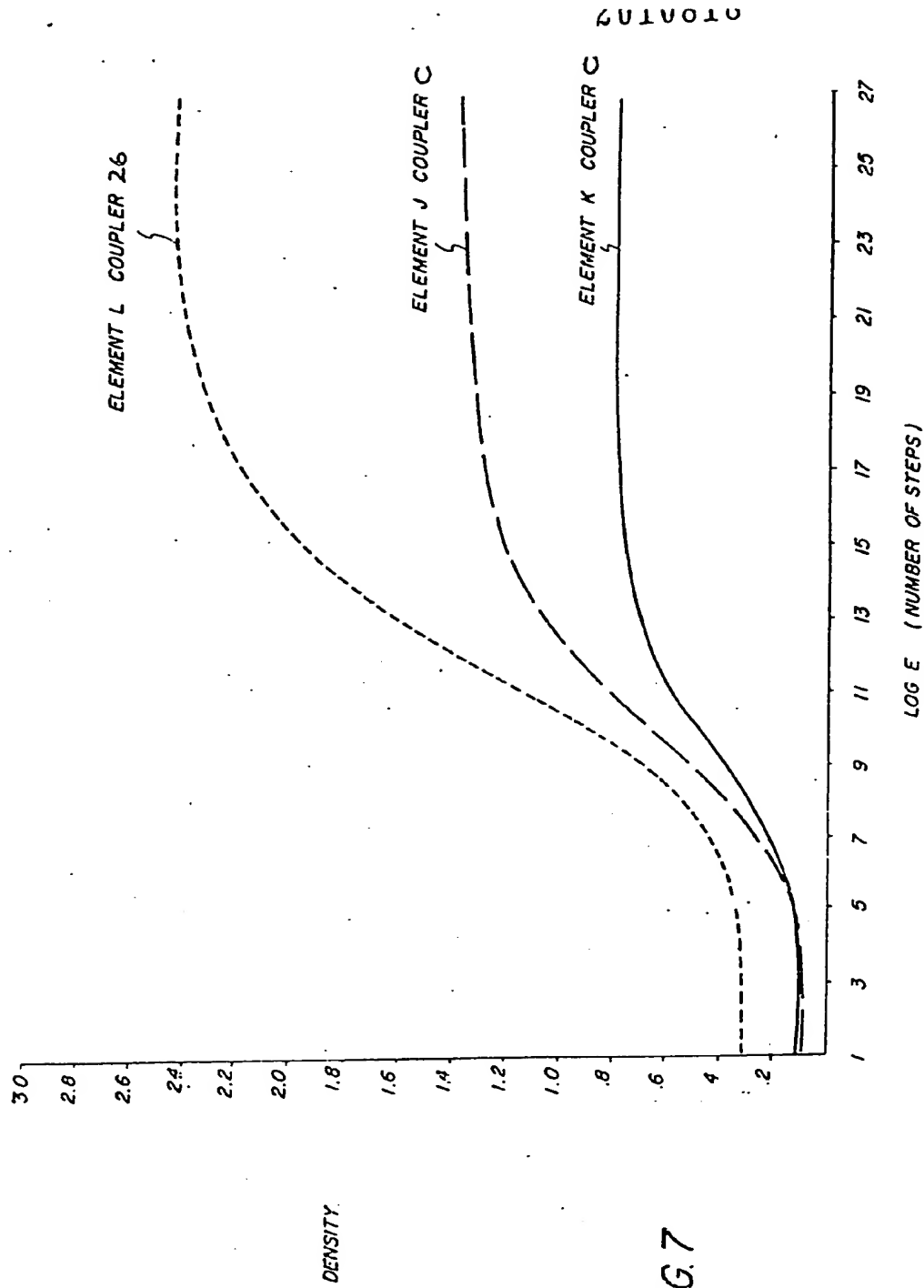


FIG. 6

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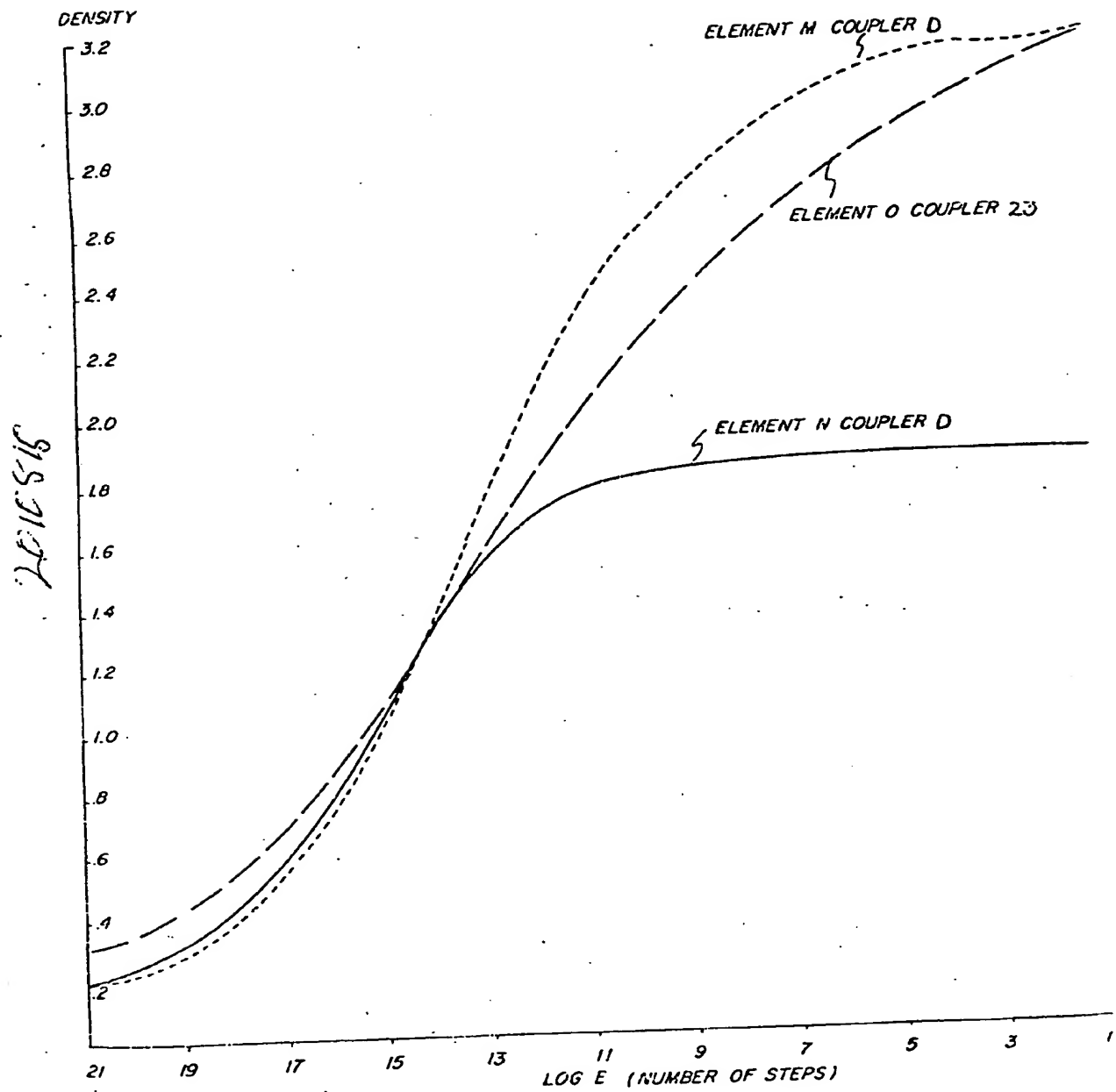


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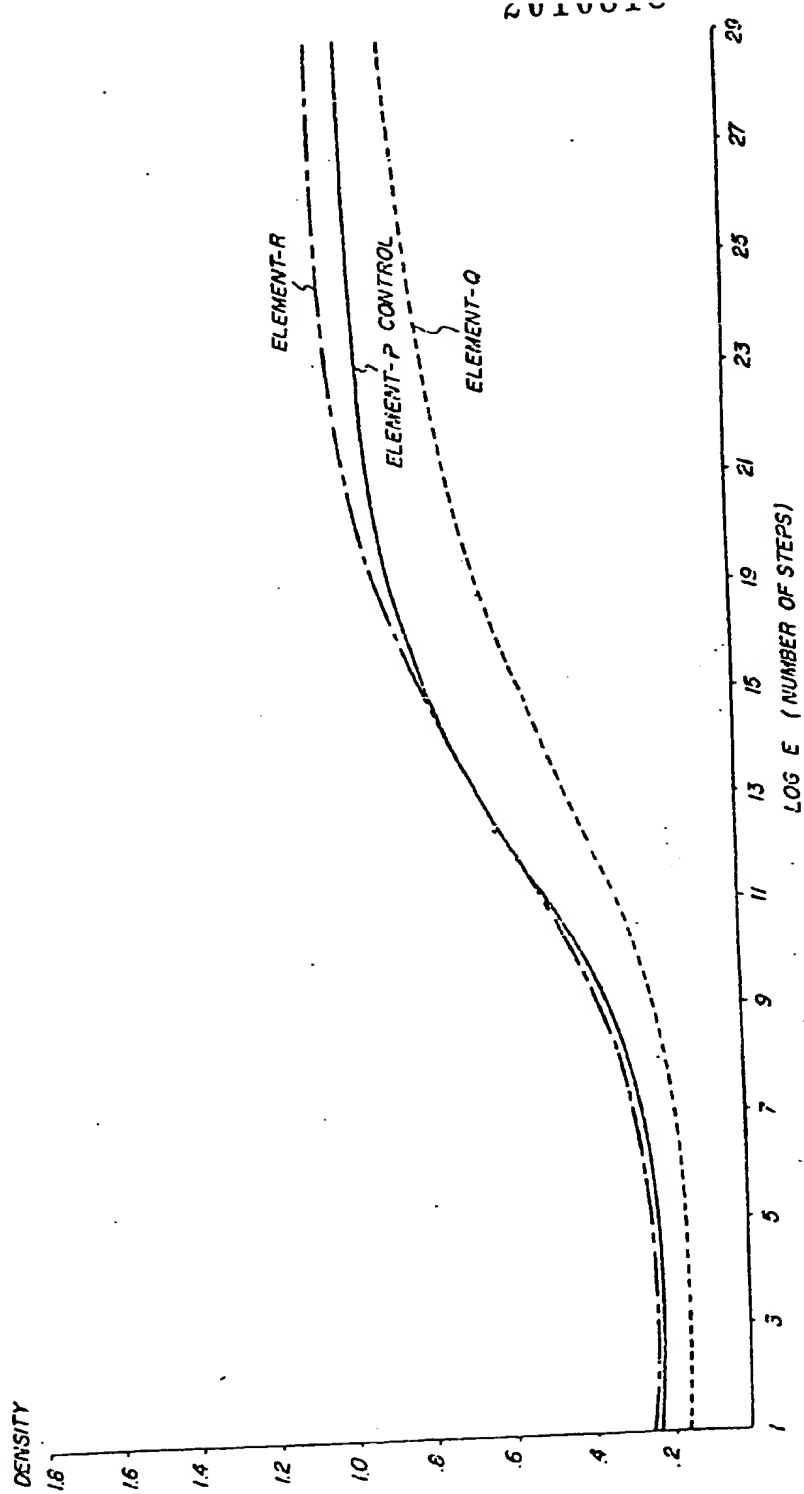
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FIG 8



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FIG. 9



SPECIFICATION

Photographic couplers with a cleavable group, photographic materials containing them and methods of forming images

This invention relates to photographic materials containing couplers which make available photographically useful compounds during photographic processing.

The art has recognized various ways in which a photographically useful compound can be released from compounds in photographic elements and processes. For example, Whitmore et al U.S. Patent 3,148,062 and Barr et al U.S. Patent 3,227,554 show the release of a development inhibitor or a dye from the coupling position of a photographic coupler upon reaction of the coupler with oxidized colour developing agent. Bloom et al U.S. Patent 3,443,940 and Bloom U.S. Patent 3,751,406 show a photographic coupler containing a dye in a non-coupling position. Reaction of the coupler with oxidized colour developing agent following by a ring closure reaction of the coupled developing agent at the point of attachment of the dye leads to release of the dye from the coupler. Holtz U.S. Patent 3,705,801 shows photographic couplers which release from the coupling position thereof a bleach inhibitor upon reaction of the coupler with oxidized colour developing agent. Fields et al U.S. Patent 3,980,479 shows compounds containing a nucleophilic group and a photographically useful group attached to the compound through an electrophilic cleavage group. When subjected to alkaline conditions the nucleophilic group and the electrophilic cleavage group interact to release the photographically useful group unless the compound has reacted with oxidized developing agent, in which event release is inhibited. British Specifications 1,464,104 and 1,464,105 and British Applications 9043/78, 9045/78 and 27/4/79 show other compounds from which a photographically useful compound is released by a nucleophilic displacement reaction during photographic processing.

A feature which these compounds and techniques of the prior art have in common is that the photographically useful compound is released directly from the compound in its useful form. Such direct release limits control over the timing and rate of release of the photographically useful compound, as well as over the rate and distance it may then travel through the material before reacting with another compound in the material. Some degree of control over these parameters may be obtained by suitably modifying one or more of: (1) the portion of the compound from which the photographically useful compound is released, (2) the means of attachment of the photographically useful compound to said portion and (3) the photographically useful compound itself. However, such modifications may be inconsistent with the end use intended and hence removes a degree of freedom in designing a compound for a given purpose. For example, modifying a photographic coupler containing a releasable development inhibitor so as to modify the rate of release of the development inhibitor may affect not only rate of release but also may affect the hue of the dye formed by the coupler and/or the reactivity or diffusivity of the development inhibitor.

Thus, there is a need for compounds that will release or otherwise make available photographically useful groups, but which will permit control over such parameters as time of release, rate of release, and rate of diffusion of the photographically useful group, without modifying the photographically useful group or the coupler group from which it is released in a way which would be inconsistent with the ultimate use for which each is intended.

According to the present invention there is provided a photographic material comprising a support, at least one photosensitive silver halide emulsion layer and associated therewith a photographic coupler comprising a coupler group and a releasable photographically useful group, characterized in that the coupler contains a timing group, joining said coupler and photographically useful groups, which is cleavable from said coupler group on reaction with oxidized colour developing agent and the resulting cleaved timing and photographically useful group entity is able to undergo an intramolecular nucleophilic displacement reaction to make available a photographically useful compound.

As used herein, the terms "coupler" and "coupler compound" refer to the entire compound, including the coupler group, the timing group and the photographically useful group; while the term "coupler group" refers to that portion of the compound other than the timing group and the photographically useful group. The term "photographically useful group" means the radical of a photographically useful compound.

The present invention also provides the above couplers per se.

The particular timing group employed, including the linkage by which it is attached to the coupler group and the nature of the substituents on it, can be varied so as to control such parameters as rate and time of cleavage of the timing group from the coupler group and of the photographically useful group from the timing group. Since these parameters can be controlled by modification of the timing group, greater freedom is allowed in selecting the coupler and photographically useful groups for a particular end use.

The photographic couplers of the present invention may, for example, be represented by the formula:



where COUP is a coupler group,
TIME is a timing group and

PUG is a photographically useful group.

The coupler group may be any coupler group employed in conventional colour-forming couplers which yield coloured products on reaction with oxidized colour developing agents as well as coupler groups which yield colourless products on reaction with oxidized colour developing agents.

- 5 The coupler group may be unballasted or ballasted with an oil-soluble or fat-tail group. It may be monomeric, or it can form part of a dimeric, oligomeric or polymeric coupler, in which case more than one -TIME-PUG group can be contained in the coupler, or it can form part of a bis compound in which the TIME or PUG group forms part of the link between two coupler groups.

- 10 Depending upon the particular coupler group, the particular colour developing agent and the type of processing, the reaction product of the coupler group and oxidized colour developing agent can be: (1) coloured and nondiffusible, in which case it will remain in the location where it is formed; (2) coloured and diffusible, in which case it may be removed during processing from the location where it is formed or allowed to migrate to a different location; or (3) colourless and diffusible or non-diffusible, in which case it will not contribute to image density. In cases (2) and (3) the reaction product may be initially coloured and/or non-diffusible but converted to colourless and/or diffusible products during the course of processing.

- 15 The -TIME-PUG group is joined to the coupler group at a position from which groups released from couplers by reaction with oxidized colour developing agent can be attached. Preferably, the -TIME-PUG group is attached to the coupling position of the coupler group so that upon reaction of the coupler with oxidized colour developing agent the -TIME-PUG group will be displaced. However, the -TIME-PUG group can be in a non-coupling position e.g. as in Bloom U.S. Patent 3,443,940 referred to above, from which position it will be displaced as a result of reaction of the coupler with oxidized colour developing agent. In the case where the -TIME-PUG group is in a non-coupling position of the coupler moiety, other groups may be in the coupling position, including conventional coupling-off groups or the same or a different photographically useful group from that contained in the -TIME-PUG group. Alternatively, the coupler group may have a -TIME-PUG group in each of the coupling position and a non-coupling position. Accordingly, couplers used in the invention can release more than one mole of photographically useful group per mole of coupler. The photographically useful groups can be the same or different and can be released at the same or different times and rates.

- 20 The intramolecular nucleophilic displacement reaction undergone by the timing group may be any of the reactions known in the chemical arts and discussed in, for example, Capon and McManus, *Neighboring Group Participation*, Vol. 1, Plenum Press, New York, 1976. As used herein, the term "intramolecular nucleophilic displacement reaction" refers to a reaction in which a nucleophilic centre of a compound reacts directly, or indirectly through an intervening molecule, at another site on the compound, which is an electrophilic centre, to effect displacement of a group or atom attached to the electrophilic centre. Preferably such compounds have a nucleophilic group and an electrophilic group spatially related to achieve reactive proximity. The preferred timing groups comprise (A) a nucleophilic group attached to the coupler group at a position from which it is displaced by oxidized colour developing agent, (B) an electrophilic group attached to the photographically useful group, and (C) a linking group spatially relating said groups (A) and (B) so that, after cleavage of (A) from the coupler group, they are able to undergo an intramolecular nucleophilic displacement reaction cleaving the photographically useful group from the timing group. Especially preferred are linking groups in which (C) is such that the nucleophilic displacement reaction leads to the formation of a 3- to 7- membered ring, preferably a 5- or 6-membered ring.

- 25 A nucleophilic group is a grouping of atoms one of which is electron rich. This electron rich atom is referred to as the nucleophilic centre. An electrophilic group is understood to be a grouping of atoms one of which is electron deficient. This electron deficient atom is referred to as the electrophilic centre.

- 30 It is preferred that the nucleophilic group contains an electron rich oxygen, sulphur or nitrogen atom. It is further preferred that the electrophilic group contains an electron deficient carbonyl, thiocarbonyl, phosphinyl or thiophosphinyl group.

- 35 Examples of nucleophilic groups are the following in which the left hand bond is joined to the coupler group:-

- O-(CR'₂)_n-, -S-(CR'₂)_n-, -SO-, -SO₂-, -OSO₂-, -NR'-SO₂-,
-OCO-(CR'₂)_n-, -O-CO-O-, -O-CS-(CR'₂)_n-, -O-CS-O-,

- 55 -NR'-CO-(CR'₂)_n-, -O-CO-NR'-, -O-NR'- and -O-PO.R'-(CR'₂)_n-

- where each R' is independently hydrogen, alkyl of 1 to 20 carbon atoms, e.g. methyl, ethyl, propyl, hexyl, decyl, pentadecyl or octadecyl, or optionally substituted aryl of 6 to 20 carbon atoms, e.g. phenyl, naphthyl, benzyl, tolyl, t-butylphenyl or carboxyphenyl and n is 0, 1, 2, 3 or 4 such that a ring is formed by the nucleophilic attack on the electrophilic centre contains 3 to 7 ring atoms. Preferably R' is hydrogen or lower alkyl of 1 to 4 carbon atoms.

- 60 Examples of electrophilic groups are the following in which the right hand bond is joined to the photographically useful group:

- 65 -(CR'₂)_n-CO-, -O(CR'₂)_n-CO-, -S(CR'₂)_n-CO-, -(CR'₂)_n-NR'-CO-,
-O(CR'₂)_n-NR'-CO-, -S(CR'₂)_n-NR'-CO-, -(CR'₂)_n-CS-

$-O-(CR'_2)_n-CS-$, $-S(CR'_2)_n-CS-$, $-(CR'_2)_n-NR'-CS-$,
 $-O(CR'_2)_n-NR'-CS-$, $-S(CR'_2)_n-NR'-CS-$, $-(CR'_2)_n-NR'-PO.R'$
 and $-(CR'_2)_n-NR'-PS.R'$ - wherein R' and n are as defined above.

The linking group (C) may be an acyclic group such as alkylene (e.g. methylene, ethylene and propylene) or a cyclic group such as an aromatic group (e.g. phenylene and naphthylene) or a heterocyclic group (e.g. furan, thiophene, pyridine, quinoline and benzoxazine). Preferably (C) is alkylene or arylene. When (C) is a cyclic group, groups (A) and (B) may be attached to the same or adjacent rings. Aromatic groups (C) in which groups (A) and (B) are attached to adjacent ring positions are particularly preferred.

In order to ensure that the photographically useful group is not released prior to release of -TIME-PUG from the coupler group, the nucleophilic centre should preferably be prevented from reacting with the electrophilic centre until such release and the electrophilic centre should preferably be resistant to external attack, e.g. hydrolysis. Premature reaction can be prevented by attaching the coupler moiety to the timing group at the nucleophilic centre, so that cleavage of -TIME-PUG from the coupler moiety unblocks the nucleophilic centre and permits it to react with the electrophilic centre, or by positioning the nucleophilic group and the electrophilic group so that they are prevented from coming into reactive proximity until release. Similarly, the photographically useful group will be attached at a position on the timing group from which it will be displaced upon reaction of the nucleophilic centre and the electrophilic centre.

Release of the photographically useful compound can involve a single reaction once the timing group is cleaved from the coupler group or it can involve sequential reactions. For example, two or more sequential intramolecular nucleophilic displacement reactions may be required within the timing group to effect release of the photographically useful compound. As another example, the timing group can have two photographically useful groups attached to different locations on the timing group so that upon release of the timing group from the coupler group the nucleophilic group first reacts with the electrophilic group joining one of the photographically useful groups to form a transient cyclic ring thereby releasing that photographically useful group and then reacts with the electrophilic group joining the second photographically useful group to release that photographically useful group. As yet another example the intramolecular nucleophilic displacement reaction may release a second coupler which contains another timing group to which the photographically useful group is joined and from which it is released after the second coupler reacts with oxidized colour developing agent.

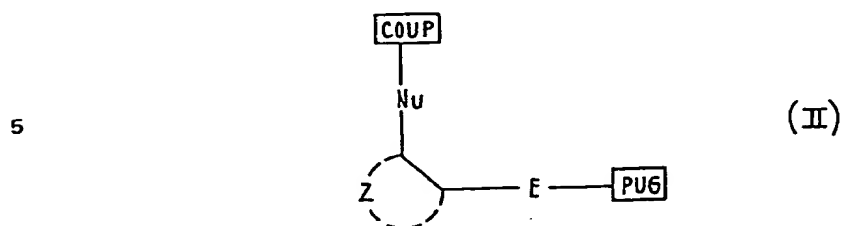
The timing group may contain groups which will permit control of one or more of the rate of reaction of COUP with oxidized colour developing agent, the rate of diffusion of -TIME-PUG once it is released from COUP and the rate of release of PUG by the intramolecular nucleophilic displacement reaction. The timing group may contain additional substituents, such as additional photographically useful groups, or precursors thereof, which will remain attached to the timing group.

It will be appreciated that for an intramolecular nucleophilic displacement reaction to occur, displacing the photographically useful group from the electrophilic group, the thermodynamics should be such that the free energy of ring closure plus the bond energy of the bond formed between the nucleophilic group and the electrophilic group is greater than the bond energy between the electrophilic group and the photographically useful group. Not all possible combinations of nucleophilic group, timing group, electrophilic group and the atom in the photographically useful group to which the electrophilic group is attached will yield a thermodynamic relationship favourable to breaking of the bond between the electrophilic group and the photographically useful group. However, it is within the skill of the art to select appropriate combinations taking the above energy relationships into account. These factors are discussed in more detail in Capon and McManus, *Neighboring Group Participation*, Volume 1, Plenum Press, New York, 1976.

The photographically useful compound may be any compound which is useful to make available in a photographic element in an imagewise fashion. The photographically useful compound may be a photographic dye or dye precursor, a development inhibitor, a development accelerator, a bleach inhibitor, a bleach accelerator, a coupler (e.g. a competing coupler, a colour-forming coupler or a development inhibitor releasing (DIR) coupler), a developing agent (e.g. a competing developing agent), a silver halide solvent or complexing agent, a toner, a hardener, a tanning agent, a fogging agent, an antifoggant, a chemical or spectral sensitizer or a desensitizer. Such dyes and photographic reagents preferably contain a hetero atom having a negative valence of 2 or 3 from group VA or Group VIA of the periodic table as set out in "Handbook of Chemistry" by Lange, 1961, pages 56-7, such as oxygen, sulphur, selenium and nitrogen (e.g., nitrogen in a heterocyclic ring). Such an atom can serve as the point on the dye or photographic reagent at which the TIME group is joined. Preferred hetero atoms in the dye or photographic reagent to which the TIME group is joined are those having a negative valence of 2 from Group VIA of the periodic table, especially sulphur and oxygen.

The photographically useful group may be present in the coupler as a performed species or in a blocked form or as a precursor. For example, a preformed development inhibitor may be attached to the timing group or the development inhibiting function may be blocked by being the point of attachment to the timing group. As another example, a preformed dye, a dye which is blocked so as to shift its spectral absorption, or a leuco dye may be attached to the timing group.

Particularly preferred couplers of the present invention are represented by the formula:



10 wherein

COUP is a coupler group,

Nu is a nucleophilic group, attached to the coupling position of COUP, of the formula $-O-CR_2$, $-O-CO-$, $-NR-CO-$, $-O-$, $-S-$, $-S-CR_2$ or $-NR-SO_2-$ in which the left hand end is attached to COUP,

Z represents the atoms necessary to complete a mono- or bicyclic aromatic or heterocyclic ring system containing 5 to 10 ring atoms which may be substituted,

E is an electrophilic group of the formula $-(CR_2)_n-CO-$, $-(CR_2)_n-NR-CO-$ or $-(CR_2)_n-CS-$ or $-(CR_2)_n-NR-CS-$ in which the right hand end is attached to PUG,

PUG is a photographically useful group,

n is 0, 1, 2, 3 or 4 such that on completion of the nucleophilic displacement reaction a ring having 5 or 6 ring members is formed, and

each R is independently, hydrogen or an alkyl group of 1-20 carbon atoms.

In Formula II, the nucleus completed by Z can be unsubstituted or substituted. The substituents can be those which will modify the rate of reaction, diffusion, or displacement, such as halogen (e.g. fluoro, chloro, bromo, iodo), nitro, alkyl of 1 to 20 carbon atoms, acyl (e.g. carboxy, carboxyalkyl, alkoxycarbonyl, alkylcarbamoyl, sulphonyl, alkylsulphonyl), ballast groups and the like, or they can be substituents which are separately useful in the photographic material, for example, a stabilizer, an antifoggant or a dye (e.g. a filter dye, a solubilized masking dye). For example, solubilizing groups will increase the rate of diffusion; ballast groups will decrease the rate of diffusion; electron withdrawing groups will decrease the rate of displacement of the photographically useful groups; while photographically useful groups which remain attached to Z can serve functions, for example stabilization or masking.

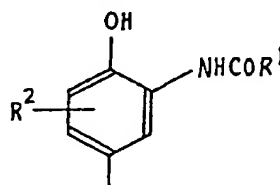
Set out below are preferred COUP, TIME and PUG groups. In these structures the unsatisfied bonds in each of the COUP and PUG show the point of attachment to TIME, the vertical unsatisfied bond in TIME shows the point of attachment of COUP and the horizontal unsatisfied bond in TIME shows the point of attachment to PUG.

35 1 COUP groups:

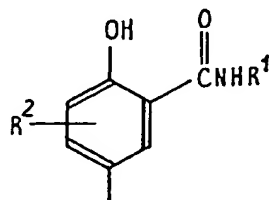
A. Couplers which form cyan dyes upon reaction with oxidized colour developing agents are described in such representative patents and publications as: U.S. Patents 2,772,162; 2,895,826, 3,002,836, 3,034,892, 2,474,293, 2,423,730, 2,367,531, 3,041,236 and "Farbkuppler-eine Literaturübersicht," published in Agfa Mitteilungen, Band II, pp. 156-175 (1961).

40 Preferably such couplers are phenols and naphthols which form cyan dyes on reaction with oxidized colour developing agent and have the -TIME-PUG group attached to the coupling position, i.e. the carbon atom in the 4-position. Structures of preferred such coupler groups are:

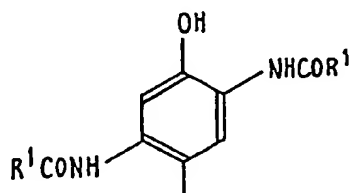
IA - 1



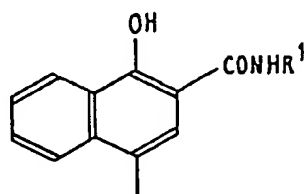
IA - 2



IA-3



IA-4

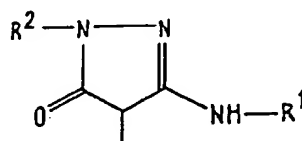


where R^1 represents a ballast group, and R^2 represents one or more halogen (e.g. chloro, fluoro), lower alkyl (e.g. methyl, ethyl, butyl) or lower alkoxy (e.g. methoxy, ethoxy, butoxy) groups.

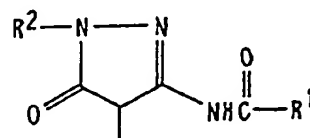
B. Couplers which form magenta dyes upon reaction with oxidized colour developing agent are described in such representative patents and publications as: U.S. Patents 2,600,788, 2,369,489, 2,343,703, 2,311,082, 3,152,896, 3,519,429, 3,062,653, 2,908,573 and "Farbkuppler-eine Literaturübersicht," published in Agfa Mitteilungen, Band II, pp. 126-156 (1961).

Preferably such couplers are pyrazolones and pyrazolotriazoles which form magenta dyes upon reaction with oxidized colour developing agents and have the -TIME-PUG group attached to the coupling position, i.e. the carbon atom in the 4-position. Structures of preferred such coupler groups are:

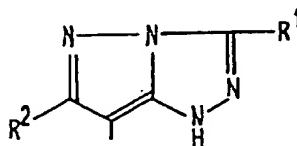
IB-1



IB-2



IB-3



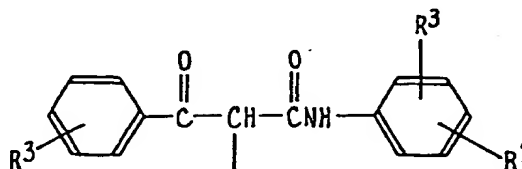
where R^1 and R^2 are as defined above for cyan coupler groups R^2 also being phenyl or substituted phenyl (e.g. 2,4,6-trihalophenyl).

C. Couplers which form yellow dyes upon reaction with oxidized and colour developing agent are described in such representative patents and publications as: U.S. Patents 2,875,057, 2,407,210, 3,265,506, 2,298,443, 3,048,194, 3,447,928 and "Farbkuppler-eine Literaturübersicht," published in Agfa Mitteilungen, Band II, pp. 112-126 (1961).

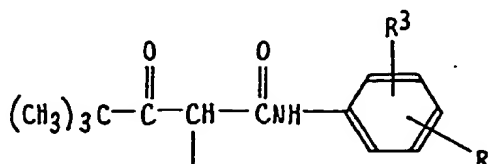
Preferably such yellow-dye forming couplers are acylacetamides, such as benzoylacetanilides and pivalyl-acetanilides, and have the -TIME-PUG group attached to the coupling position, i.e. the active methylene carbon atom.

Structures of preferred such coupler groups are:

IC-1



IC-2

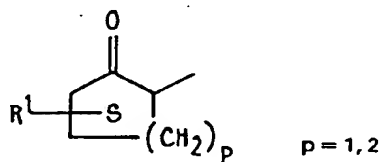


where R¹ is as defined above for cyan coupler groups and R³ is hydrogen or one of more halogen, lower alkyl (e.g. methyl, ethyl) or ballast (e.g. alkoxy of 16 to 20 carbon atoms) groups.

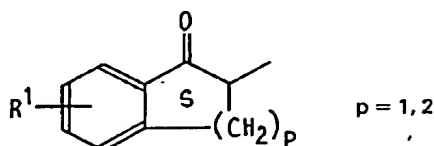
D. Couplers which form colourless products upon reaction with oxidized colour developing agent are described in such representative patents as: U.K. Patent 861,138, U.S. Patents 3,632,345, 3,928,041, 3,958,993 and 3,961,959. Preferably such couplers are cyclic carbonyl-containing compounds which form colourless products on reaction with oxidized colour developing agent and have the —TIME—PUG group attached to the carbon atom in the α-position with respect to the carbonyl group.

Structures of preferred such coupler groups are:

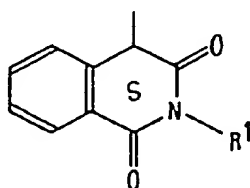
ID-1



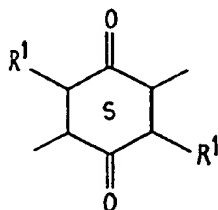
ID-2



ID-3



ID-4



where R¹ is as defined above for cyan coupler groups.

E. Couplers which form black or neutral density dyes upon reaction with oxidized colour developing agent are described in such representative patents and patent applications as U.S. Patents 1,939,231,

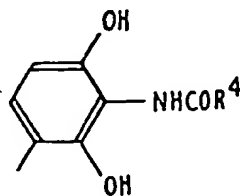
2,181,944, 2,333,106, British Patent Application No. 26843/78, (Serial No. 2003617) German OLS 2,644,194 and German OLS 2,650,764.

Preferably such couplers are resorcinols or m-aminophenols which form black or neutral products on reaction with oxidized colour developing agent and have the -TIME-PUG group para to a hydroxy group.

5 Structures of preferred such coupler groups

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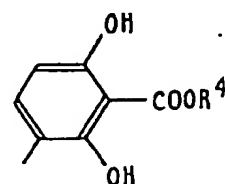
IE - 1



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IE - 2

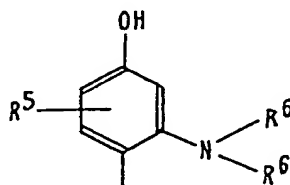


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IE - 3



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where R⁴ is alkyl of 3 to 20 carbon atoms, phenyl or phenyl substituted with hydroxy, halo, amino, alkyl of 1 to 20 carbon atoms or alkoxy of 1 to 20 carbon atoms; each R⁶ is independently hydrogen, halogen, alkyl of 1 to 20 carbon atoms, alkenyl of 1 to 20 carbon atoms, or aryl of 6 to 20 carbon atoms; and R⁵ is one or more halogen, alkyl of 1 to 20 carbon atoms, alkoxy of 1 to 20 carbon atoms or other monovalent organic groups.

35

II TIME groups:

A. Acyclic TIME groups:

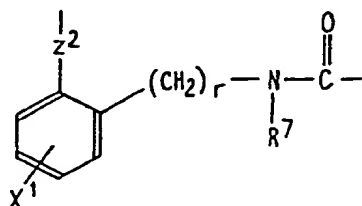
40 IIA-1 -Z¹(CH₂)_q-NR⁷-C-

40

where q is 1-4, preferably 2 or 3, Z¹ is -O-, -O-CO- or -S-, (right hand bond to (CH₂)_q), and R⁷ is hydrogen, alkyl of 1 to 20 carbon atoms, preferably lower alkyl of 1 to 4 carbon atoms, or aryl of 6 to 20 carbon atoms.

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II B - 1



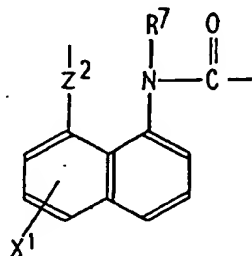
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II B - 2



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where r is 0 or 1; Z² is -O-, -O-CH₂-, -O-CO-, -NH-SO₂- or -NH-CO- (right hand bond to the ring shown), R⁷ is as defined above for acyclic TIME groups; and X¹ is hydrogen, cyano, fluoro, chloro, bromo, iodo, nitro,

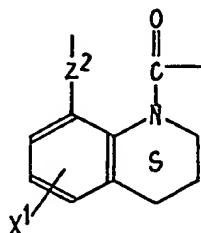
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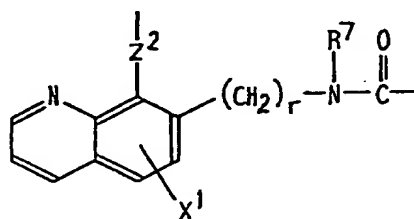
alkyl of 1 to 20 carbon atoms, a dye radical, $-\text{OR}^8$, $-\text{COOR}^8$, $-\text{CONHR}^8$, $-\text{NHCOR}^8$, $-\text{NHSO}_2\text{R}^8$, $-\text{SO}_2\text{NHR}^8$ or SO_2R^8 where R^8 is hydrogen or alkyl of 1 to 20 carbon atoms preferably alkyl of 1 to 4 carbon atoms.

C. Heterocyclic TIME groups:

II C-1



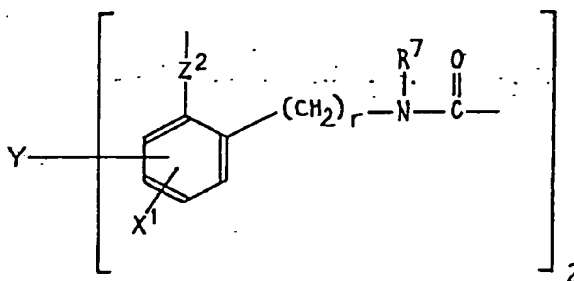
II C-2



where r , Z^2 , X^1 and R^7 are as defined above for aromatic TIME groups.

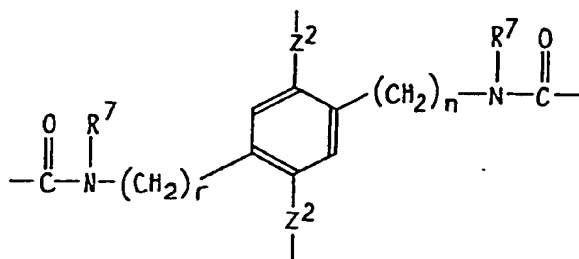
D. Bis TIME groups:

II D-1



where Y is a linking group, such as $-\text{CO}-$, $-\text{SO}_2-$ or $-\text{NHSO}_2\text{CH}_2\text{SO}_2\text{NH}-$; r , X^1 , Z^2 and R^7 are as defined above for aromatic TIME groups.

II D-2



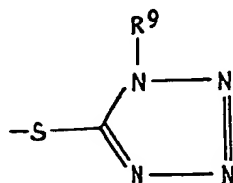
where r , Z^2 and R^7 are as defined above for aromatic TIME groups.

III PUG Groups:

A. PUG groups which form development inhibitors upon release from TIME are described in such representative patents as U.S. Patents 3,227,554; 3,384,657; 3,615,506; 3,617,291, 3,733,201 and U.K. Patent 1,450,479. Preferred development inhibitors are iodide and heterocyclic compounds such as mercaptotetrazoles, selenotetrazoles, mercaptobenzo-thiazoles, selenobenzo-thiazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles, benzotriazoles and benzodiazoles. Structures of preferred development inhibitor radicals are:

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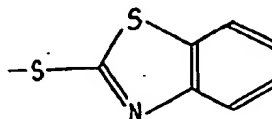
III A-1



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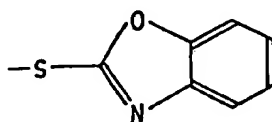
III A-2



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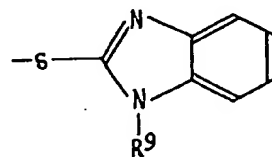
III A-3



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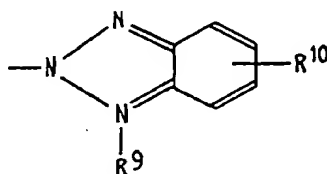
III A-4



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III A-5



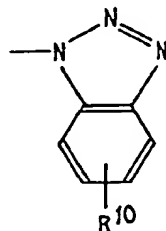
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III A-6



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50 where R^9 is hydrogen, alkyl of 1 to 8 carbon atoms (e.g. methyl, ethyl, butyl), phenyl or substituted phenyl, and R^{10} is hydrogen or one or more halogen (e.g. chloro, fluoro, bromo), or lower alkyl of 1 to 4 carbon atoms or nitro groups.

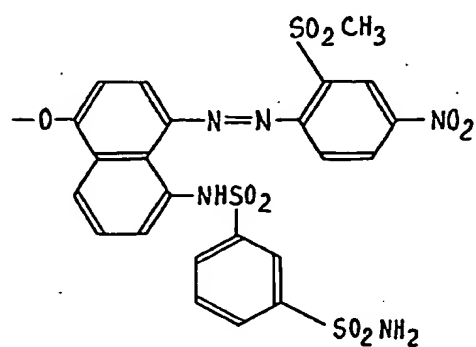
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B. PUG groups which are, or form, dyes upon release from -TIME-:

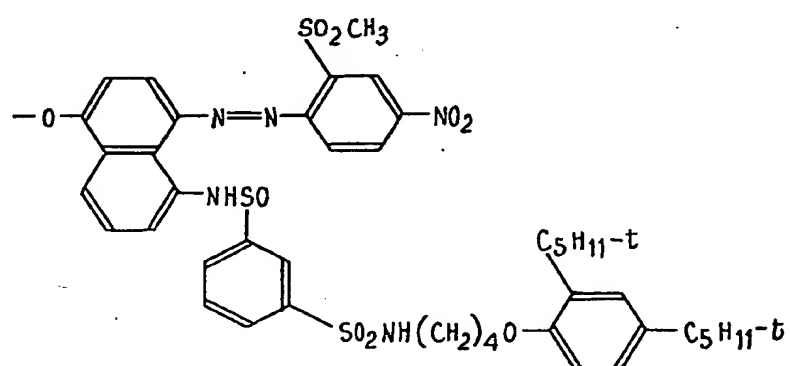
55 Suitable dyes and dye precursors include azo, azomethine, azopyrazolone, indoaniline, indophenol, anthranquinone, triarylmethane, alizarin, nitro, quinoline, indigoid and phthalocyanine dyes or precursors of such dyes such as leuco dyes, tetrazolium salts or shifted dyes. These dyes can be metal complexed or metal complexable. Representative patents describing such dyes are U.S. Patents 3,880,658; 3,931,144; 3,932,380; 3,932,381 and 3,942,987. Preferred dyes and dye precursors are azo, azomethine and indoaniline dyes and dye precursors. Structures of some preferred dye and dye precursor radicals are:

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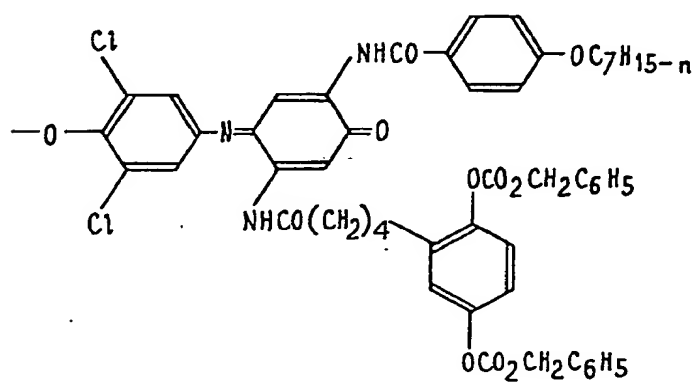
III B-1



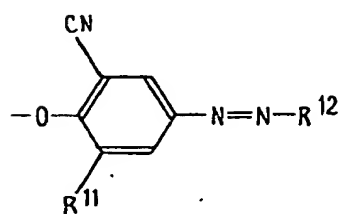
III B-2



III B-3



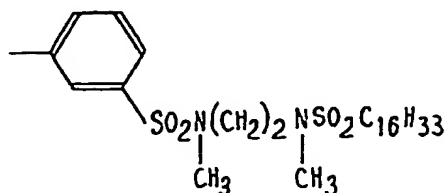
III B-4



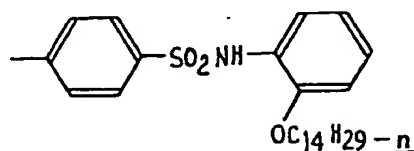
where

 R^{11} R^{12}

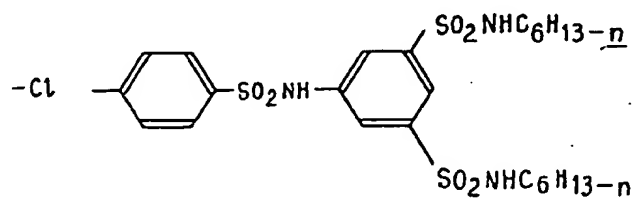
-H



-Cl



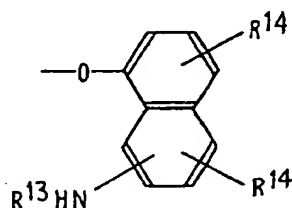
-Cl



30 C. PUG groups which are couplers:

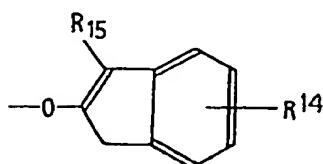
Couplers released from TIME groups can be non-diffusible colour forming couplers, non-colour forming couplers or diffusible competing couplers. Representative patents and publications and preferred structures for the first two categories are shown above in IA to IE. Representative patents and publications describing competing couplers are: "On the Chemistry of White Couplers," by W. Püschel, Agfa-Gevaert AG Mitteilungen aus der Forschungs-laboratorium der Agfa-Gevaert AG, Springer Verlag, 1954, pp. 352-367; U.S. Patents 2,998,314, 2,808,329, 2,689,793, 2,742,832; German Patent 1,168,769 and British Patent 907,274. Structures of preferred competing couplers are:

III C-1



where R^{13} is hydrogen or alkylcarbonyl (e.g. acetyl) and R^{14} is hydrogen or a solubilizing group (e.g. sulfo, aminosulphonyl carboxy, etc.).

III C-2



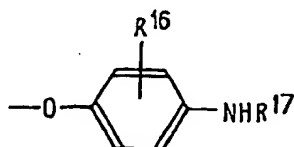
where R^{14} is as defined above and R^{15} is halogen, aryloxy, arylthio, or a development inhibitor, such as a mercaptotetrazole (e.g. phenylmercaptotetrazole or ethyl mercapto-tetrazole) radical.

60 D. PUG groups which form developing agents;

Developing agents released from TIME groups can be colour developing agents, black-and-white developing agents or cross-oxidizing developing agents. They include aminophenols, phenylene diamines, hydroquinones and pyrazolidones. Representative patents describing such development agents are: U.S. Patents 2,193,015, 2,108,243, 2,592,364, 3,656,950, 3,658,525, 2,751,297, 2,289,367, 2,772,282, 2,743,279, 2,753,265 and 2,304,953.

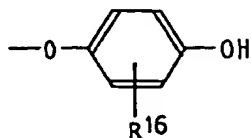
Structures of preferred developing agent radicals are:

III D-1



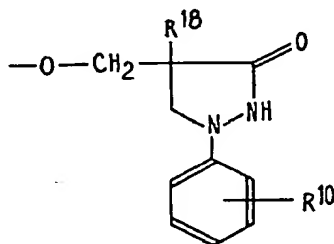
where R^{17} is hydrogen or lower alkyl of 1 to 4 carbon atoms and R^{18} is hydrogen or one or more halogen (e.g. chloro, bromo) or lower alkyl (e.g. methyl, ethyl, butyl) groups.

III D-2

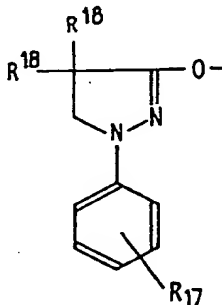


where R^{16} is as defined above

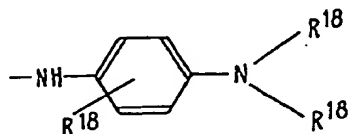
III D-3



III D-4



III D-5

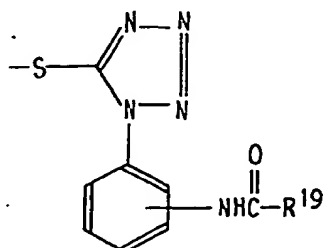


where R^{17} is as defined above and R^{18} is hydrogen, lower alkyl of 1 to 4 carbon atoms (e.g. methyl, ethyl) lower hydroxyalkyl of 1 to 4 carbon atoms (e.g. hydroxymethyl, hydroxyethyl) or lower sulphaalkyl.

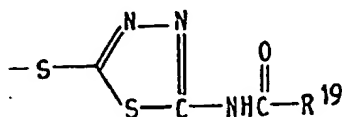
E. PUG groups which form bleach inhibitors:

Representative patents are U.S. Patents 3,705,801, 3,715,208 and German OLS 2,405,279. Structures of preferred bleach inhibitor radicals are:

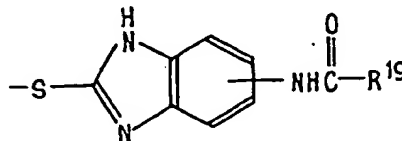
III E-1



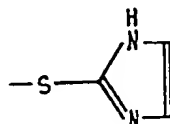
III E-2



III E-3



III E-4



where R¹⁹ is an alkyl group of 6 to 20 carbon atoms.

Typically, the couplers of the invention are prepared by attaching to the appropriate coupler group, or a derivative of the coupler group, the nucleophilic and linking groups. The linking group will have, in the appropriate spatial relationship to the nucleophilic group, a derivative of the electrophilic group, or another functional group, which will form the electrophilic group when the photographically useful group is attached. This is then reacted with an appropriate derivative of the photographically useful compound to form the desired coupler. The examples which follow show the way in which these steps can be performed using specific reactants and reactions.

The photographic couplers of the invention can be incorporated in photographic materials associated with silver halide, or in photographic processing solutions, such as developer solutions, so that upon development of an exposed photographic material they will be in reactive association with oxidized colour developing agent. Coupler compounds incorporated in photographic processing solutions should be of such molecular size and configuration that they will diffuse through photographic layers with the processing solution. When incorporated in a photographic material, the coupler compounds should be non-diffusible, i.e. they should be of such molecular size and configuration that they will not significantly diffuse or wander from the layer in which they are coated.

Photographic materials of this invention may be processed by conventional techniques in which colour image forming couplers and colour developing agents are incorporated in separate processing solutions or compositions or in the material. The materials may be processed by redox amplification techniques in which developed or latent image silver acts as a catalyst for oxidation of the colour developing agent by an oxidizing agent such as a transition metal complex (i.e. cobalt (III) hexammine) or a peroxide (e.g. hydrogen peroxide). Amplification processing is described, for example, in U.S. Patents 3,674,490; 3,822,129; 3,834,907; 3,841,873; 3,847,619; 3,862,842; 3,902,905 and 3,923,511.

Photographic materials of this invention can be simple elements comprising a support and a single silver halide emulsion layer or they can be multilayer, multicolour materials. The coupler compounds used in the invention may be incorporated in the silver halide emulsion layer or in another layer, such as an adjacent layer, where they will come into reactive association with oxidized colour developing agent which has developed silver halide in the emulsion layer. The silver halide emulsion layer may contain, or have associated with it, other photographic coupler compounds, e.g. colour image forming couplers or coloured masking couplers. These other photographic coupler compounds can form dyes of the same or different colour as the present photographic coupler compounds. Additionally, the silver halide emulsion layer(s) may contain addenda conventionally contained in such layers.

A typical multilayer, multicolour photographic material according to this invention comprises a support having thereon a red-sensitive silver halide emulsion unit having associated therewith a cyan dye image providing material, a green-sensitive silver halide emulsion unit having associated therewith a magenta dye image providing material and a blue-sensitive silver halide emulsion unit having associated therewith a yellow dye image-providing material, at least one of the silver halide emulsion units having associated therewith a photographic coupler of the present invention. Each silver halide emulsion unit can be composed of one or more layers and the various units and layers can be arranged in different locations with respect to one another. Typical arrangements are described in U.S. Patents 3,227,554; 3,620,747; 3,843,369; and U.K. Patents 923,045 and 1,500,497. The coupler compounds of the invention may be incorporated in or associated with one or more layers or units of the material.

The light sensitive silver halide emulsions may include coarse, fine, regular or non-regular grain silver halide crystals or mixtures thereof and may be comprised of such silver halides as silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver chlorobromiodide and mixtures thereof. The emulsions may be negative working or direct-positive emulsions. They may form

latent images predominantly on the surface of the silver halide grains or predominantly in the interior of the silver halide grains. They may be chemically and spectrally sensitized. The emulsions typically will be gelatin emulsions although other hydrophilic colloids may be used in accordance with usual practice.

The support may be any suitable support used with photographic materials. Typical supports include
 5 cellulose nitrate film, cellulose acetate film, polyvinylacetate film, polyethylene terephthalate film, polycarbonate film and related films or resinous materials as well as glass, paper and metal. Typically, a flexible support is employed, such as a polymeric film or paper support. Paper supports may be acetylated or coated with baryta and/or an α -olefin polymer, particularly a polymer of an α -olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene or ethylene-butene copolymers.

10 Further details regarding silver halide emulsions and elements, and addenda incorporated therein can be found in *Research Disclosure*, December 1971, Item 9232, Paragraphs I through XVIII. *Research Disclosure* is published by Industrial Opportunities Ltd., Homewell, Havant, Hampshire, PO9 1EF, United Kingdom.

The photographic couplers of the invention may be used in photographic materials in the same ways that
 15 known photographic couplers which release photographically useful groups were used. However, because of the improved ability to control the release of the photographically useful group, the present couplers permit enhanced effects or more selective effects than heretofore possible. In addition, the present couplers may be employed in applications where conventional couplers have previously been employed and a separate component was employed to provide a photographically useful group.

20 Depending upon the nature of the particular photographically useful group, the couplers may be incorporated in the photographic material for different purposes and in different locations and these materials may contain various other components. Reference will be made to exemplary ways in which preferred photographically useful groups may be incorporated.

When the photographically useful group released from the coupler is a development inhibitor, it may
 25 be employed in a photographic material as described, for example, in U.S. Patents 3,227,554; 3,620,747; 3,703,375 and U.S. Patent Application Serial No. 758,251 filed January 10, 1977. Other patents and applications describing ways in which couplers which release development inhibitors can be employed are U.K. Patent 1,460,991; U.S. Patent 3,892,572 and German OLS 2,516,982. Couplers of the invention which release a development inhibitor may be contained in, or in reactive association with, one or more of the
 30 silver halide emulsion units in a colour photographic material. If the silver halide emulsion unit is composed of more than one layer, one or more of such layers may contain the coupler. The layers may contain other photographic couplers conventionally used in the art. The present couplers may form dyes of the same colour as the colour forming coupler(s) in the layer or unit, they can form a dye of a different colour, or they can result in a colourless or neutral reaction product. The range of operation of the development inhibitor between layers when released from the present couplers may be controlled by the
 35 use of scavenger layers, e.g. a layer of a fine grain silver halide emulsion. Scavenger layers may be in various locations in a material containing the present couplers, including between layers, next to the support, or over all of the layers.

The present couplers which release development inhibitors can enhance the effects heretofore
 40 obtained with DIR couplers since they can release a development inhibitor at a distance from the point at which oxidized colour developing agent reacted with the coupler.

Thus, such present couplers can provide enhanced interlayer interimage effects and enhanced interlayer chemical adjacency effects. The couplers provide a degree of control over the effects obtainable from DIR couplers which heretofore could not be attained.

45 The photographic couplers of the invention which release bleach inhibitors may be employed in the ways described in U.S. Patent 3,705,801, to inhibit the bleaching of silver in selected areas of a photographic material.

The photographic couplers of the invention which release a dye or dye precursor may be used in
 50 processes where the dye is allowed to diffuse to an integral or separate receiving layer to form a desired image as described for example in U.S. Patents 3,227,551; 3,443,940 and 3,751,406. Alternatively, the dye may be retained in the location where it is released to augment the density of the dye formed from the coupler from which it is released or to modify or correct the hue of that dye or another dye. In another embodiment, the dye may be completely removed from the material and the dye which was not released from the coupler may be retained in the material as a colour correcting mask.

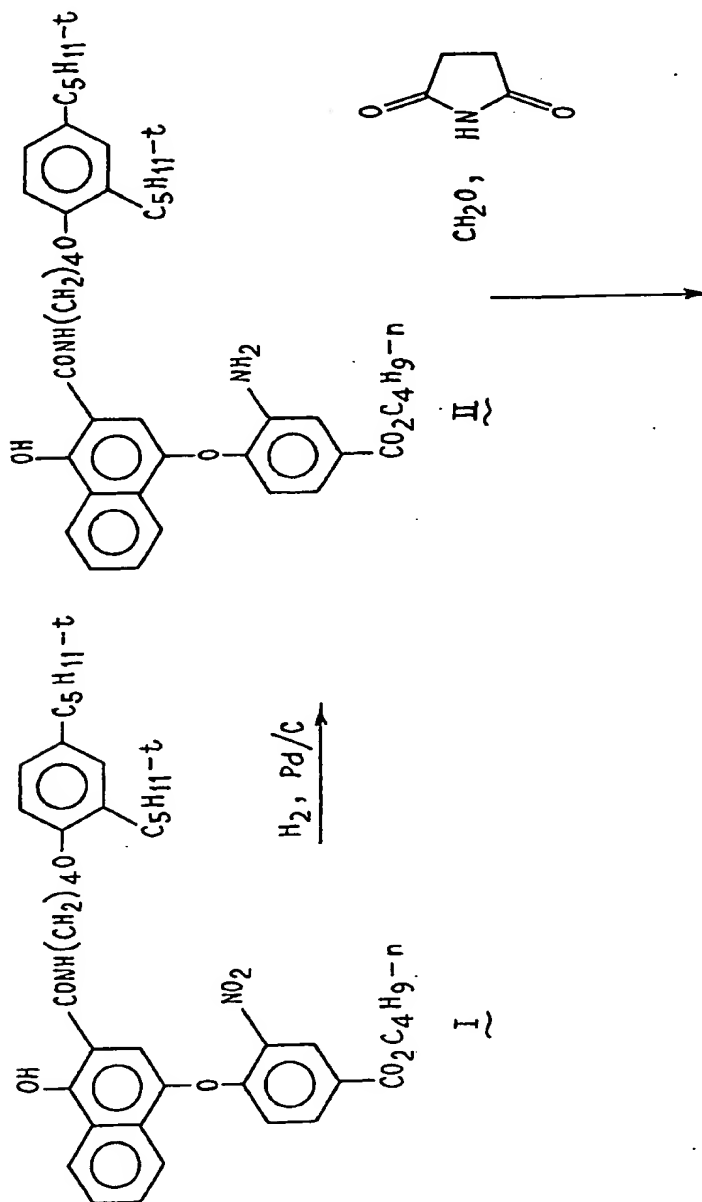
55 The couplers of the invention in which the photographically useful groups is a coupler radical can be employed to release another coupler. If the released coupler is a dye-forming coupler it can react with oxidized developing agent in the same or an adjacent layer to form a dye of the same or a different colour or hue as that obtained from the primary coupler. If the released coupler is a competing coupler it can react with oxidized colour developing agent in the same or an adjacent layer to reduce dye density.

60 The photographic couplers of the invention in which the photographically useful group is a developing agent radical can be used to release a developing agent which will compete with the colour forming developing agent, and thus reduce dye density. Alternatively, they can provide, in an imagewise manner, a developing agent which because of such considerations as activity would not desirably be introduced into the element in a uniform fashion.

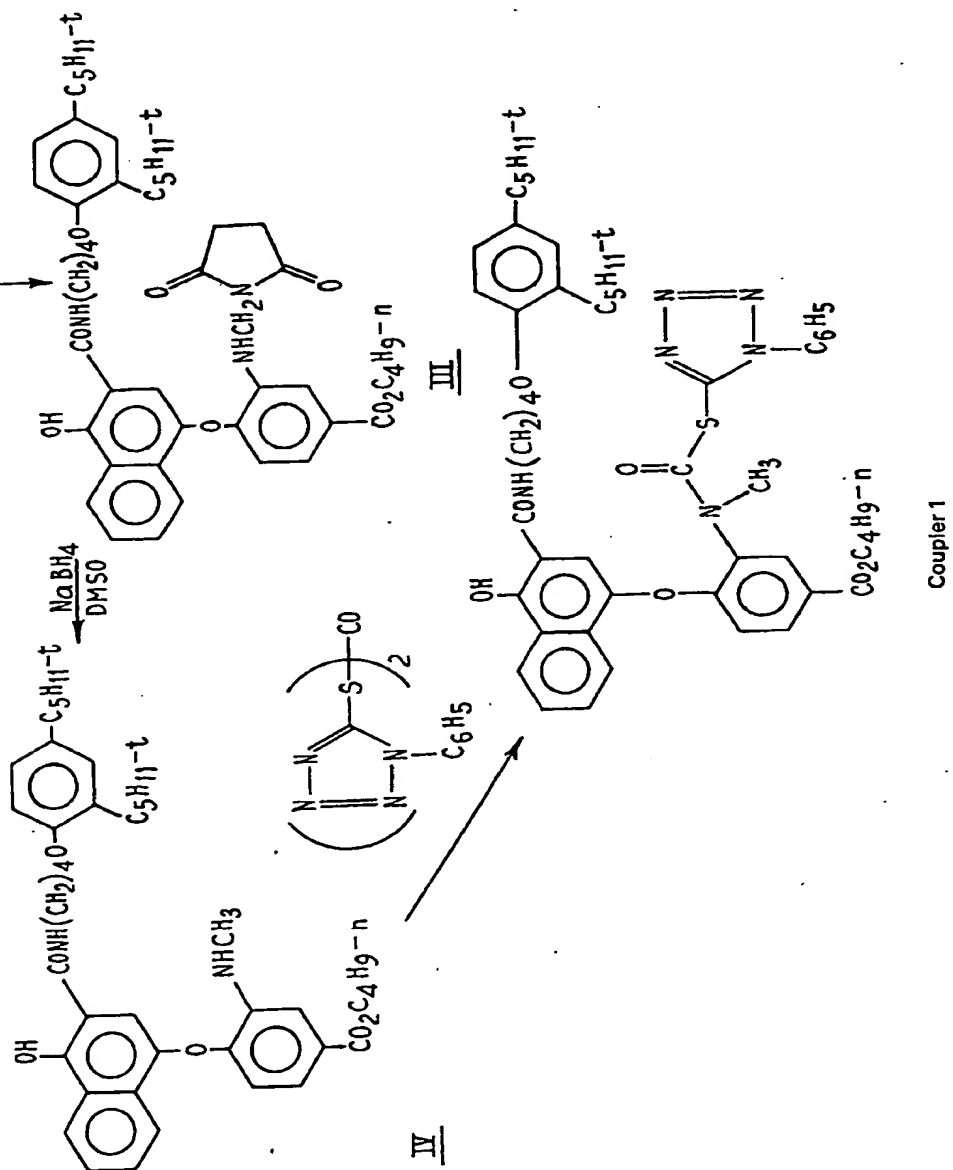
65 The following Preparative Examples and Examples illustrate the preparation and photographic use of

the couplers of the present invention. Certain results are illustrated graphically in the accompanying drawings.

Preparative Example 1 -- Preparation of a Cyan Coupler which Releases A Development Inhibitor:



Preparative Example 1 (continued)



Preparation of Compound II

In a 1-litre stainless steel Parr hydrogenation vessel was placed 100 g (0.14 mol) of compound I, 1.0 g of 10% Pd/C catalyst, and 500 ml ethyl acetate. The mixture was reduced under 40 p.s.i. of hydrogen at ambient temperature. After the theoretical uptake of hydrogen, the catalyst was removed and solvent
 5 evaporated *in vacuo*. The crude product was recrystallized from acetonitrile to give 67 g (70%) of white crystalline solid; m.p. 174–175°C.

Preparation of Compound III

A 500 ml 3-neck round bottom flask was charged with 50 g (0.073 mol) of compound II, 14.5 g (0.15 mol)
 10 of succinimide, 11.9 ml (0.15 mol) of formalin, and 250 ml ethanol. The reaction mixture was heated on a steam bath for 30 hours. After cooling, the mixture was poured into 1200 ml water and 60 ml ethyl acetate, with thorough stirring. The organic phase was separated, dried over magnesium sulphate, and the sol-
 15 vent evaporated *in vacuo*. The crude residue was taken up in a minimum amount of benzene and chromatographically separated with a silica-gel column using benzene and ethyl acetate as eluants. The fractions containing the product were combined and the solvent evaporated *in vacuo*. The solid residue was recrystallized from hexane giving 30.4 g (53%) of pure colourless crystalline product; m.p. 102–105°C.

Preparation of Compound IV

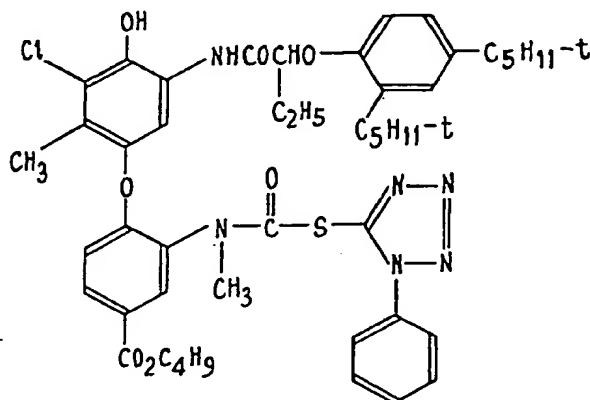
To a stirred solution of 30.4 g (0.04 mol) of compound III in 250 ml dimethyl sulphoxide was added
 20 portionwise 1.8 g (0.05 mol) of sodium borohydride, maintaining the temperature below 40°C. After stirring for an additional 30 minutes, the mixture was poured into water and extracted with ethyl acetate. The organic extracts were combined, washed with brine, dried over magnesium sulphate and the solvent
 25 evaporated *in vacuo*. The residue was taken up in a minimum amount of benzene and eluted with benzene-ethyl acetate mixtures through a silica-gel column. The fractions containing the product were combined and evaporated *in vacuo*. The residue was recrystallized from hexane giving 15.5 g (60%) of white crystalline material; m.p. 144–146°C.

Preparation of Coupler 1

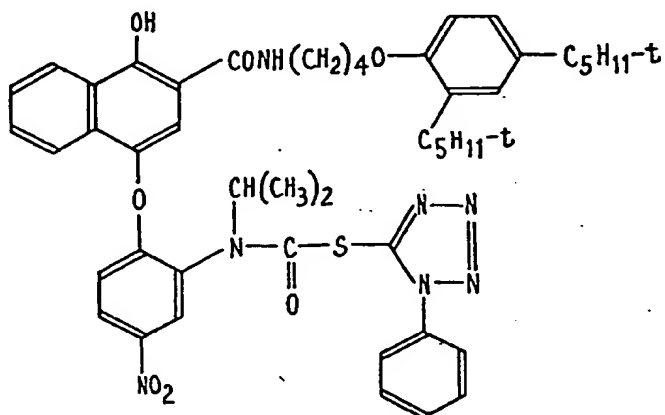
To a stirred solution of 7.0 g (0.01 mol) of compound IV in 35 ml of tetrahydrofuran (THF) was added
 30 dropwise under a nitrogen atmosphere 12 ml (1.0 M solution in THF) of S,S'-carbonyl-di-l-phenyl-5-mercaptotetrazole. The reaction mixture was stirred for 2 hours, poured into ice-water and extracted with ethyl acetate. The extracts were dried over magnesium sulphate and evaporated *in vacuo*. The pale
 35 yellow residue was recrystallized from ethyl acetate-ligroin yielding 5.0 g (56%) of pure colourless long needles; m.p. 114–117°C.

Using similar reaction procedures the following couplers were prepared:

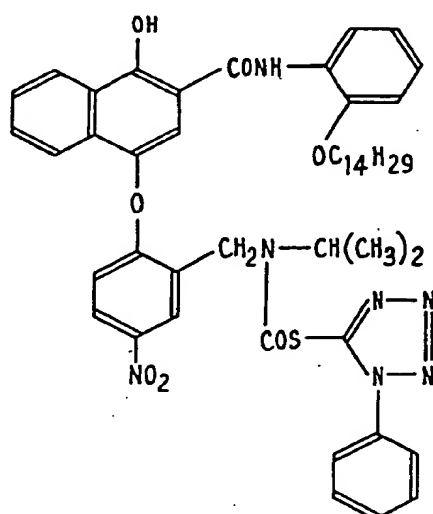
Coupler 2



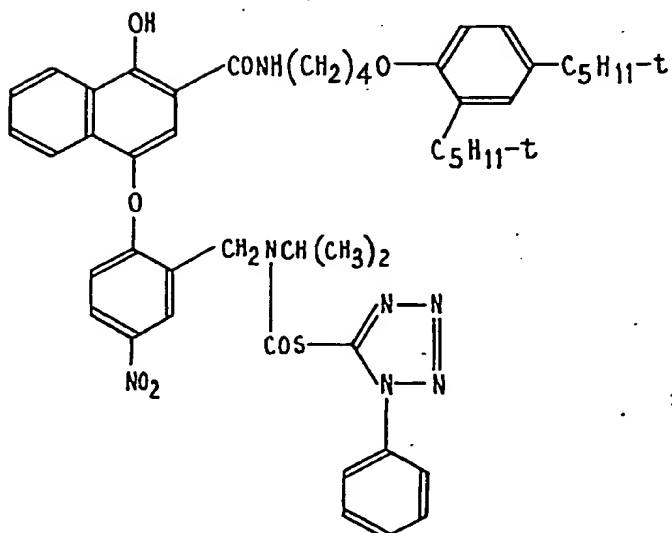
Coupler 3

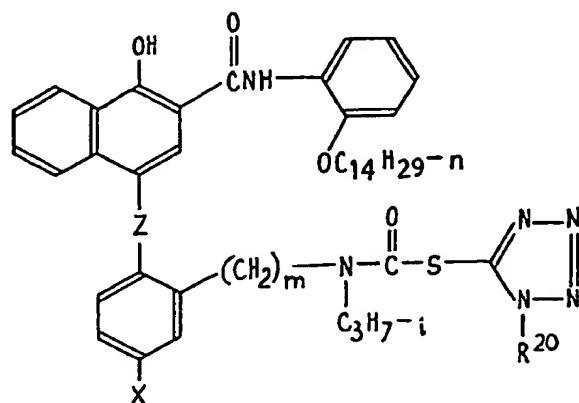


Coupler 4

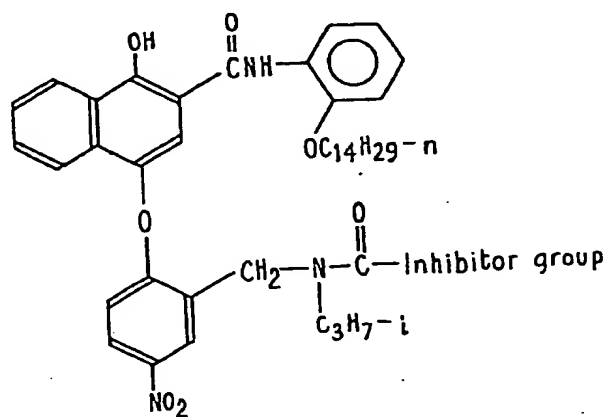


Coupler 5





Coupler No.	Z	X	m	R ²⁰
6	O	NO ₂	0	
7	S	NO ₂	1	
8	O	NO ₂	1	
9	O	NO ₂	1	
10	O	NO ₂	1	
11	O	NHSO ₂ C ₄ H ₉	0	
12	O	NHSO ₂ C ₈ H ₁₇	1	
13	S	H	0	



Coupler No.

Inhibitor Group

14

Ethylmercaptotetrazolyl

15

n-Butylmercaptotetrazolyl

16

Cyclohexylmercaptotetrazolyl

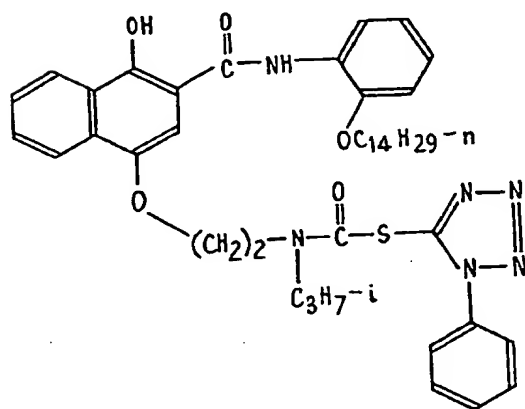
17

N-Heptylmercaptotetrazolyl

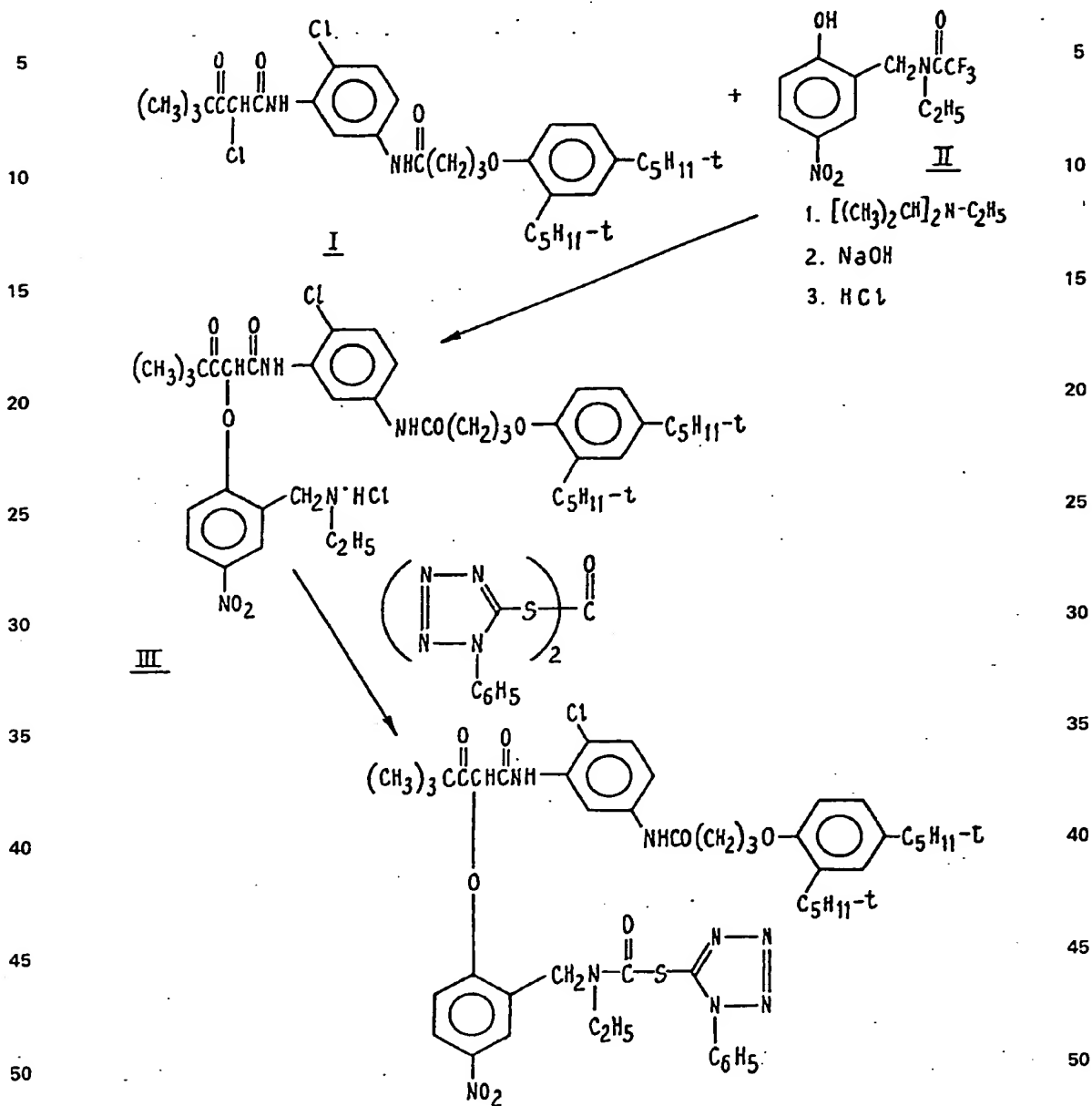
18

5,6-Dichlorobenzotriazolyl

Coupler 19



Preparative Example 2 -- Preparation of a Yellow Coupler Which Releases A Development Inhibitor:



Coupler 20

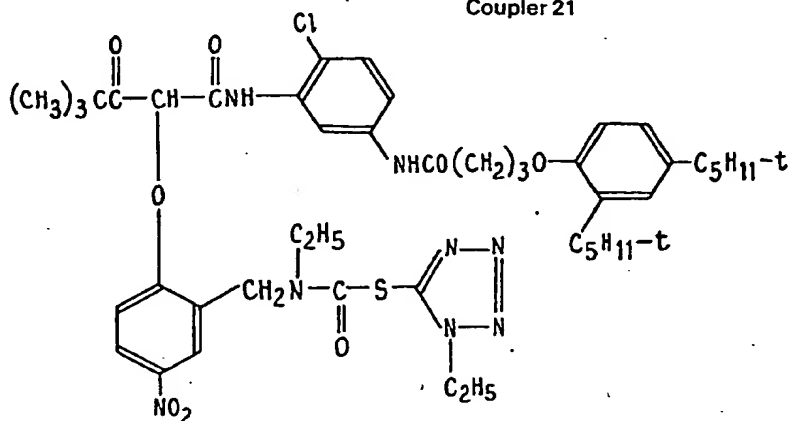
Preparation of Compound III

To a solution of 16.0 g (0.055 mol) of 2-N-ethyl trifluoroacetamido-methyl-4-nitrophenol in 250 ml acetonitrile was added with stirring 7.10 g (0.055 mol) of di-isopropyl ethylamine and 30.4 g (0.050 mol) of α -pivalyl- α -chloro- [2-chloro-5-(2,4-di-tert-amylphenoxy)butylamido]acetanilide. The mixture was heated on a steam bath for 1-1/2 hours. The solvent was evaporated *in vacuo* yielding a yellow oil. The oil was taken up in 200 ml of methanol and reacted with a solution of 20 g (0.5 mol) of sodium hydroxide in 50 ml of water. After stirring for 1 hour, the dark red solution was poured into 800 ml of ice water and 200 ml of concentrated hydrochloric acid. The solid was collected, triturated with ethyl acetate and then washed with diethyl ether. Yield of the desired amine hydrochloride salt was 35.8 g (89%); m.p. 184-186°C.

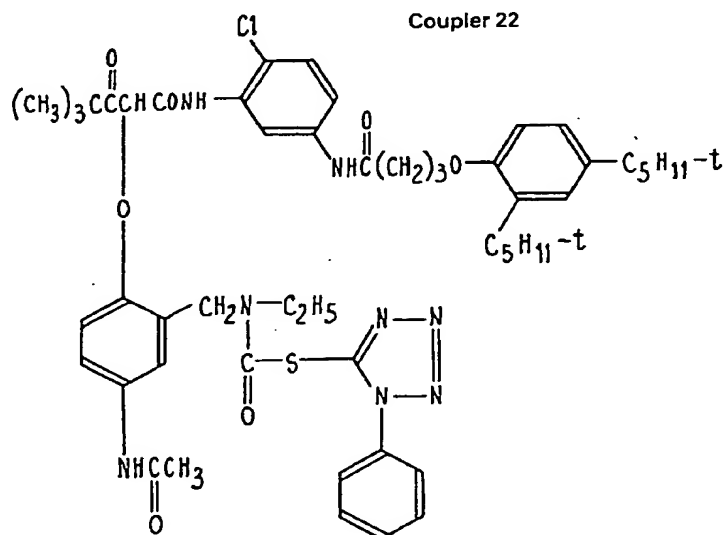
Preparation of Coupler 20

To a mixture of 18.5 g (0.023 mol) of compound III suspended in 300 ml of ethyl acetate was added with vigorous stirring 150 ml of a saturated sodium bi-carbonate solution. When all the solid had dissolved, the organic phase was separated, dried over magnesium sulphate and filtered. To the filtrate was added with stirring 8.8 g (0.023 mol) of S,S'-carbonyldi-1-phenyl-5-mercaptotetrazole prepared by bubbling phosgene into a benzene solution of 1-phenyl-5-mercaptotetrazole. The reaction mixture was stirred for 30 minutes after which the solvent was evaporated *in vacuo*. The residue was chromatographically separated with a silica-gel column using hexane-ethyl acetate mixtures as eluents. The fractions containing the pure product were combined and evaporated *in vacuo* to give 10 g (45%) of Coupler 20; m.p. 77-80°C.

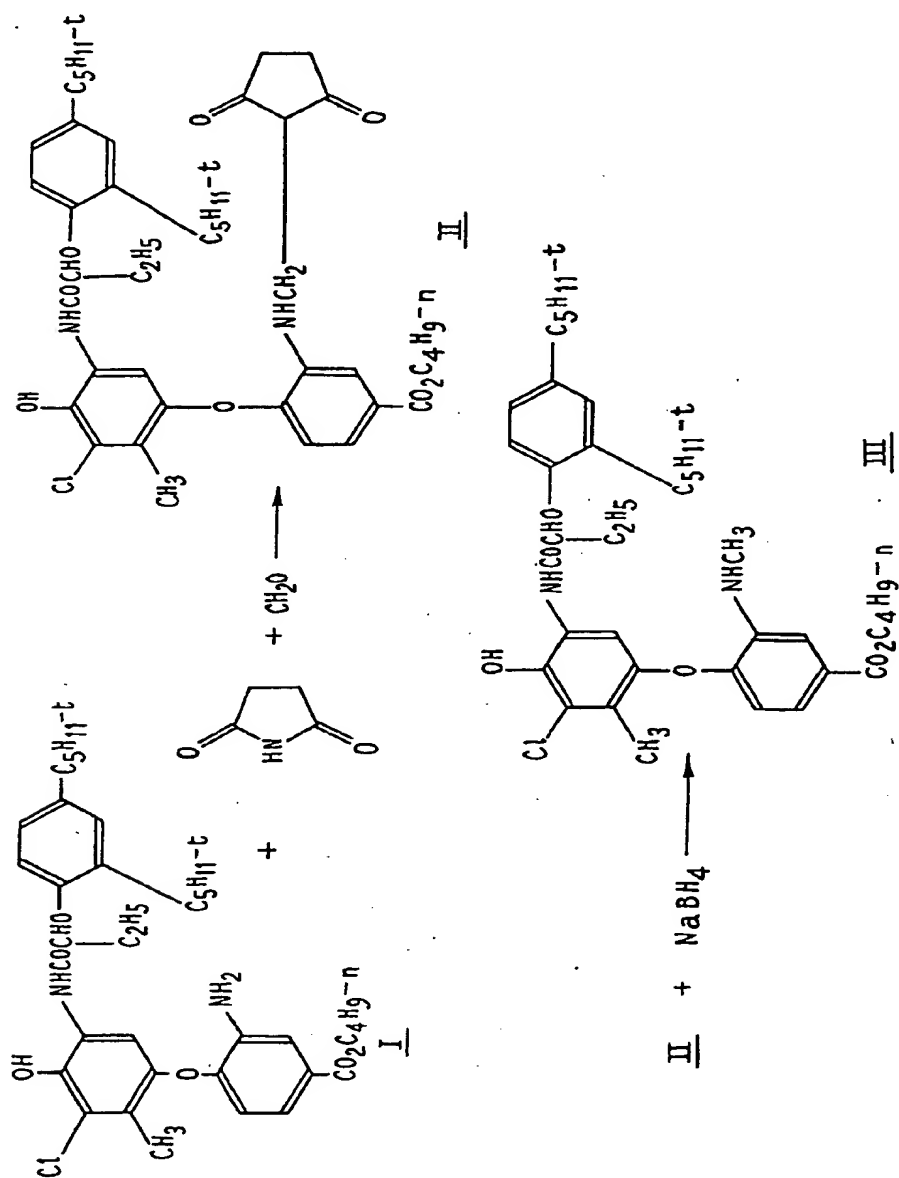
Using a similar reaction procedure, Coupler 21 was prepared.

Coupler 21

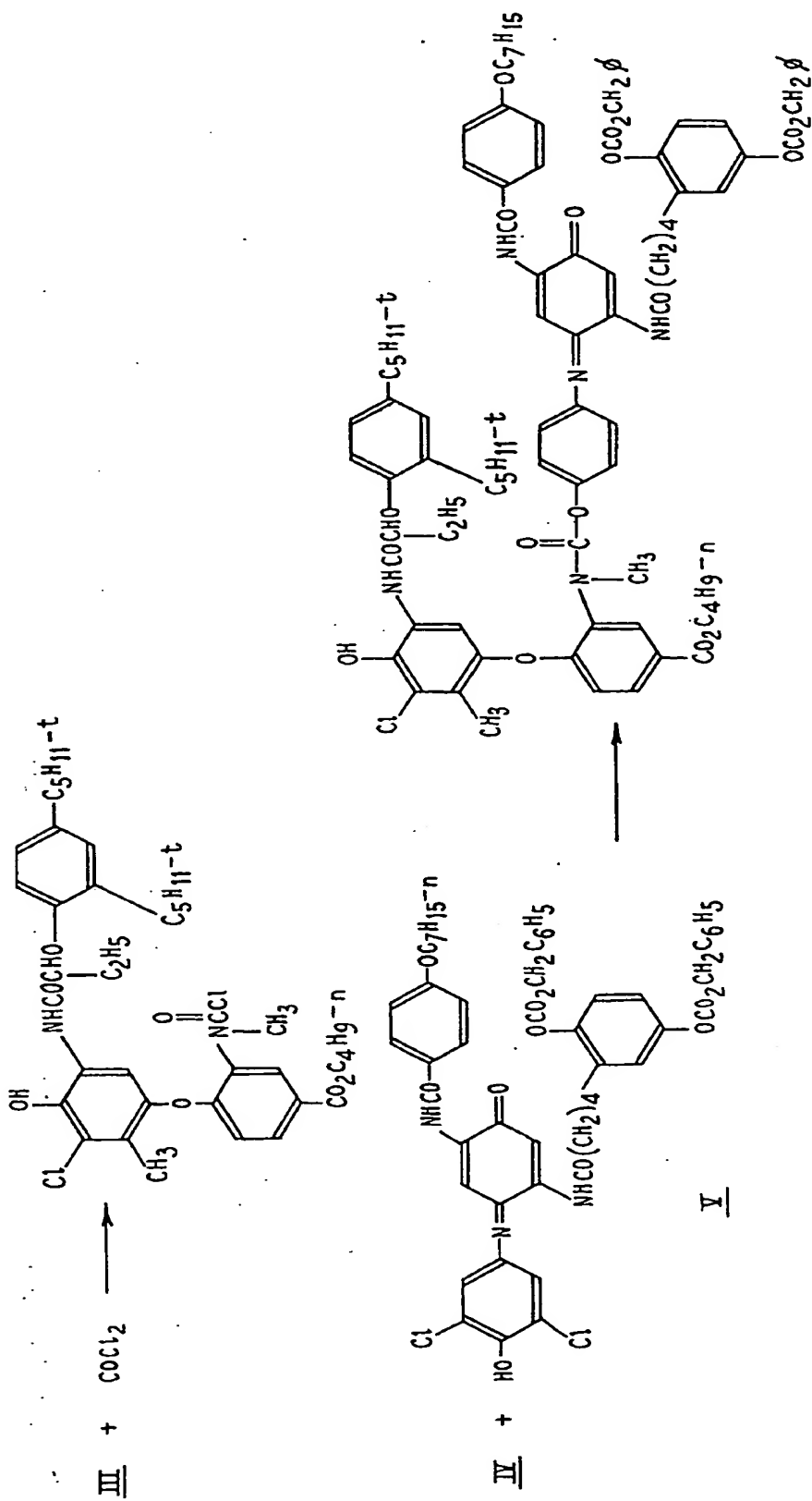
Coupler 22 was prepared by the catalytic reduction of Coupler 20 using 10% Pd/C and reacting the resulting amine with acetic anhydride; m.p. 115-117°C.

Coupler 22

Preparative Example 3—Preparation of a Cyan Coupler Which Releases a Cyan Dye:



Preparative Example 3 (continued)



Preparation of Compound III

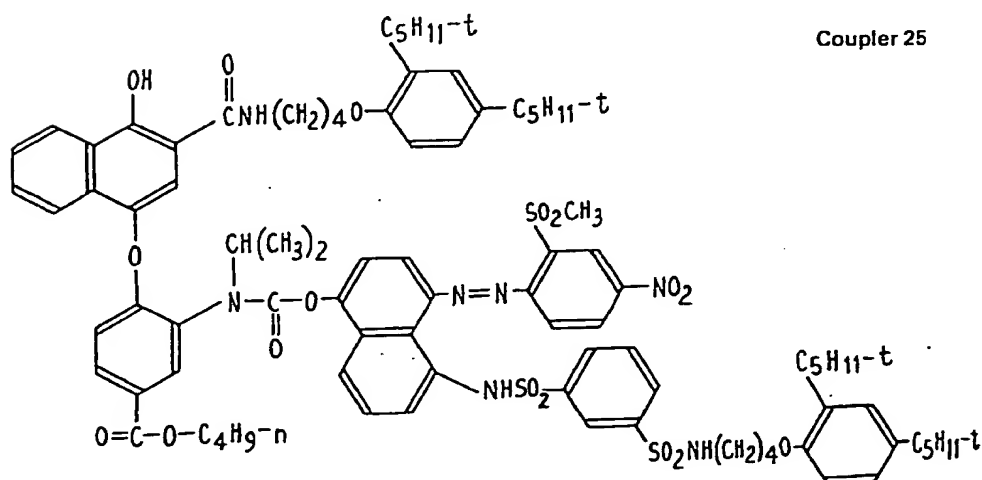
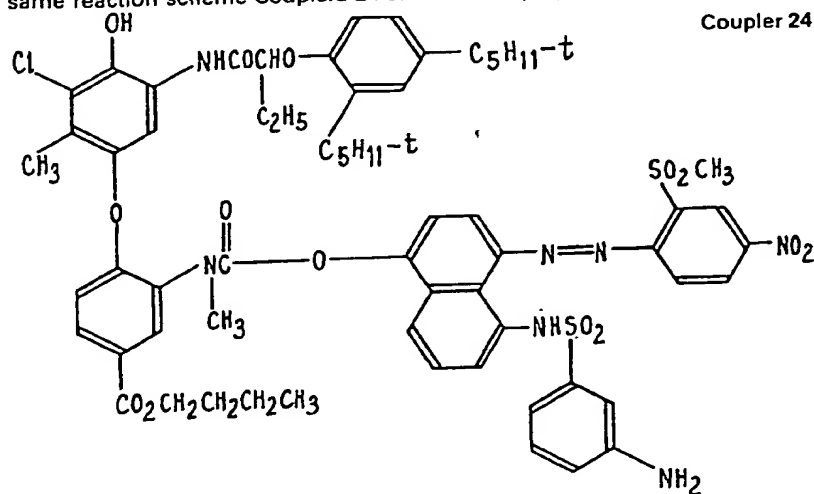
To a mixture of 26.7 g of compound 1, 5.3 g of succinimide, 10 drops of trifluoroacetic acid and 240 ml of di-n-butyl ether heated at 100–110°C, was added with stirring 1.7 g of paraformaldehyde. After heating for 1.5 hours, the mixture was cooled and the solvent was removed on a rotary evaporator. The residue was taken up in dichloromethane and passed through a silica gel column to give 20 g of the succinimide-methyl derivative II.

The product obtained above was dissolved in 100 ml of dimethylsulphoxide and warmed to 40°C. With stirring, 4.0 g of sodium borohydride was added in portions. It was then heated on a steam bath for 1.5 hours. The mixture was cooled and poured cautiously with stirring into 1.2 litres ice-water and 40 ml acetic acid. The white solid was collected, dissolved in 600 ml of dichloromethane, dried over MgSO_4 , filtered and the filtrate passed through a short silica gel column using dichloromethane as the eluant. The solvent was removed under reduced pressure, and the residue was recrystallized from acetonitrile to give 10.7 g of pure compound III.

Preparation of Coupler 23

To a solution 4.1 g of compound III in 60 ml of dried benzene was added with stirring 50 ml of 12% solution of phosgene in benzene. The mixture was stirred at room temperature for 3 hours. The solvent was removed under reduced pressure. The carbamoyl chloride derivative IV thus obtained was dissolved in 20 ml tetrahydrofuran and added to a solution of 5.9 g of indophenol dye V in 50 ml of dried pyridine. The reaction mixture was stirred at room temperature for one hour and then heated on a steam bath overnight. The solvent was removed under reduced pressure giving an orange residue. It was taken up in benzene, and chromatographically separated with a silica gel column eluting first with benzene, then with benzene-ethyl acetate solvent mixtures. The fractions containing the pure coupler were combined and the solvent removed *in vacuo* to give 2.6 g of coupler 23.

Using the same reaction scheme Couplers 24 and 25 were prepared:



Preparation of Compound V

To a stirred solution of 7.62 g of sulphanilic acid in 40 ml 2N hydrochloric acid was added dropwise, at 0-5°C, an ice-cold solution of 3.04 g of NaNO₂ in 20 ml water. The diazonium salt solution thus obtained was added dropwise to a solution of 6.14 g of 2-cyano-6-chlorophenol in 50 ml pyridine, maintaining the reaction temperature below 10°C. After the addition, the mixture was allowed to warm up slowly to room temperature, stirred for 2 more hours, and then cooled in an ice bath. The bright yellow solid which separated out was collected, washed with ice-cold water followed by cold acetone. Yield of the crude yellow azo dye was 15.4 g.

The product obtained above was added in small portions to a stirred solution of 500 g of thionyl chloride and 100 ml N,N-dimethylformamide at 0-5°C. The mixture was stirred at this temperature for 4 hours and then poured into ice water. The orange solid which separated out was collected, washed twice with cold dilute hydrochloric acid and dried, dissolved in 700 ml ethyl acetate, dried over Na₂SO₄, filtered, and the solvent removed under reduced pressure to give 13 g of product; m.p. 209-211°C.

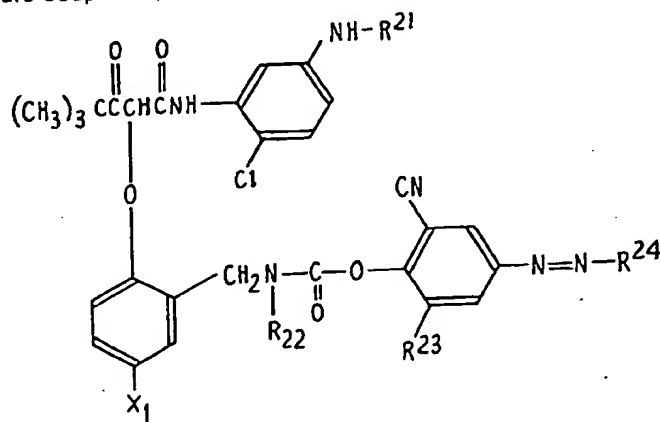
The azophenol sulphonyl chloride derivative was added with stirring to a solution of 16 g of 2-tetradecyl-oxyaniline in 300 ml tetrahydrofuran and 50 g of di-iso-propylethylamine at 0-5°C. After the addition, the mixture was stirred at room temperature for 2 hours. It was poured into ice-water containing 100 ml concentrated hydrochloric acid. The solid was collected, washed with water, and dried. The crude dye was dissolved in 50 ml CHCl₃ and chromatographically separated with a silica gel column using a CHCl₃-ethyl acetate-acetic acid solvent mixture as eluant. A yield of 12 g of pure Compound V was obtained; m.p. 98-100°C.

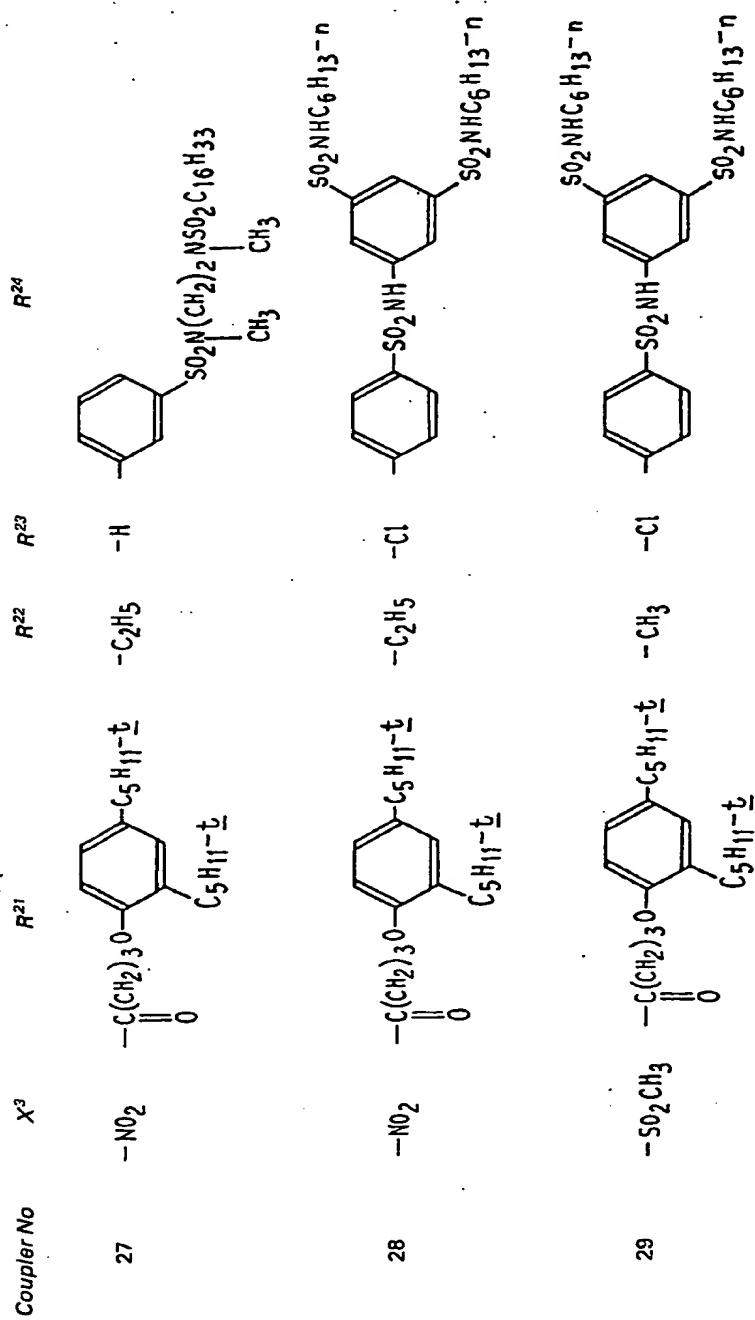
Preparation of Coupler 26

To a suspension of 12 g of Compound III of Example 2 in 500 ml benzene was added with stirring 100 ml of saturated NaHCO₃ solution. After stirring for 3 hours the organic phase was separated, dried over MgSO₄, filtered and the filtrate concentrated under reduced pressure to 100 ml. With stirring, 100 g of 12% solution of phosgene in benzene was added. The reaction mixture was stirred overnight, after which it was concentrated to dryness under reduced pressure. The residue was taken up in 20 ml tetrahydrofuran and reacted with 10.3 g of azophenol dye V dissolved in 500 ml pyridine. The reaction mixture was stirred at room temperature over the weekend.

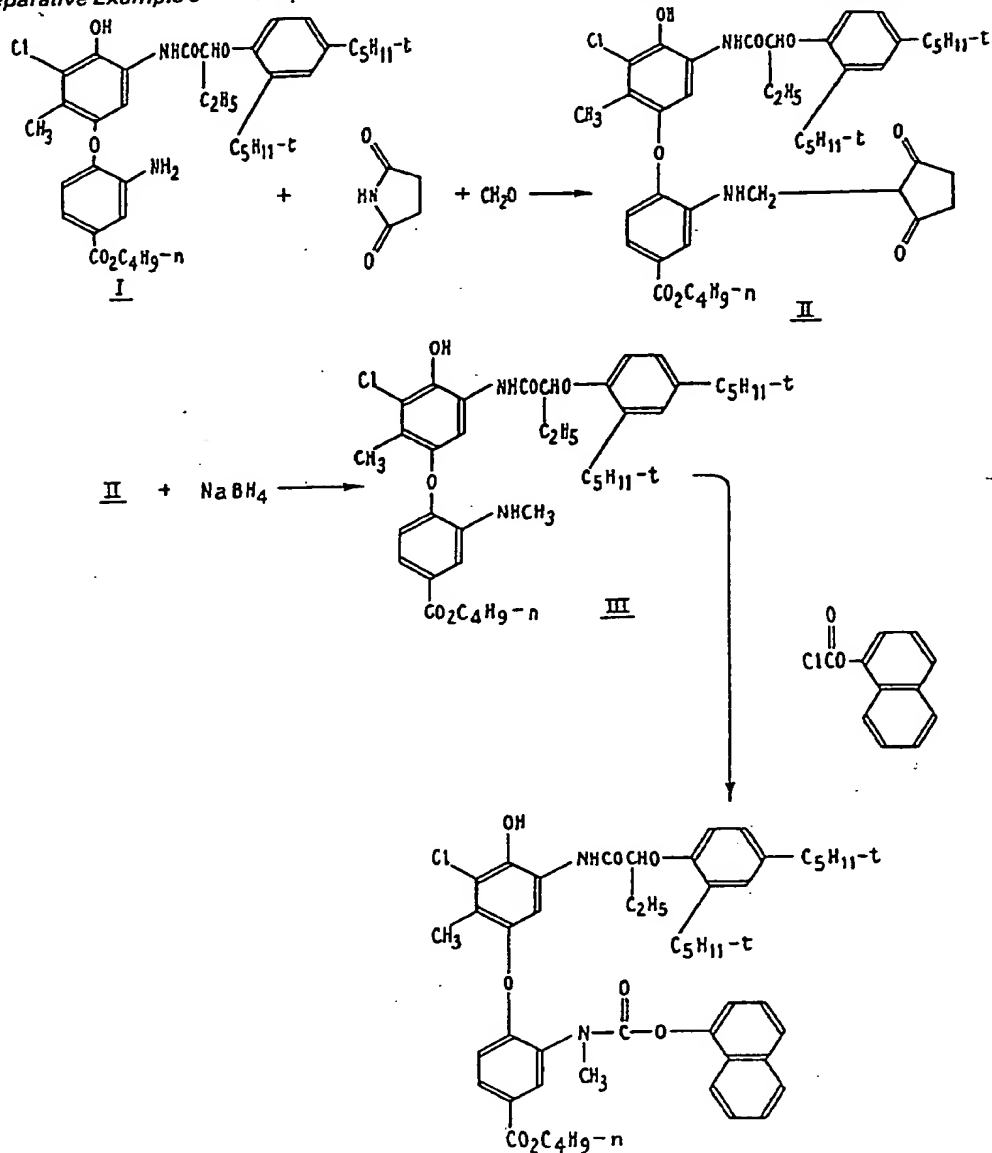
It was poured into ice-water containing 60 ml concentrated hydrochloric acid. The brown solid was collected, washed with water, and dried. The crude coupler was dissolved in a minimum amount of CHCl₃ and purified by passing through a silica gel column using CHCl₃ and ethyl acetate as eluants. Yield of pure Coupler 26: 9.2 g; m.p. 107-110°C.

Using a similar procedure Coupler 27, 28 and 29 were prepared:





Preparative Example 5 — Preparation of a cyan coupler which releases a competing coupler



Preparation of compounds II and III

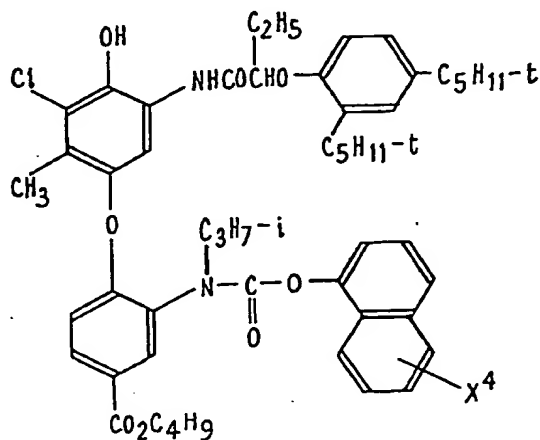
To a mixture of 26.7 g of compound I, 5.3 g of succinimide, 10 drops of trifluoroacetic acid and 240 ml of di-n-butyl ether heated at 100–110°C, was added with stirring 1.7 g of paraformaldehyde. After heating for 1.5 hours, the mixture was cooled and the solvent was removed. The residue was taken up in dichloromethane and passed through a silica gel column to give 20 g of the succinimidomethyl derivative, compound II.

Compound II was dissolved in 100 ml of dimethyl-sulphoxide and warmed to 40°C. With stirring, 4.0 g of sodium borohydride was added in portions. It was then heated on a steam bath for 1.5 hours. The mixture was cooled and poured cautiously with stirring into 1.2 litres of ice water and 40 ml acetic acid. The white solid was collected, dissolved in 600 ml of dichloromethane, dried over MgSO_4 and filtered. The filtrate was passed through a short silica gel column using dichloromethane as the eluant. The solvent was removed under reduced pressure, and the residue was recrystallized from acetonitrile to give 10.7 g of pure compound III.

Preparation of Coupler 30

To a stirred solution of 4.6 g of compound III and 1.14 g of quinoline in 50 ml of tetrahydrofuran was added a solution of 1.6 g of 1-naphthylchloroformate in 20 ml tetrahydrofuran. The reaction mixture was stirred at ambient temperature for 3 hours, then poured into ice water containing 5 ml of concentrated 5 HCl. The solid was collected, washed with water and dried. Recrystallization from acetonitrile gave 4.8 g of Coupler 30; m.p. 197–199°C.

Using a similar procedure couplers 31 to 34 were prepared.



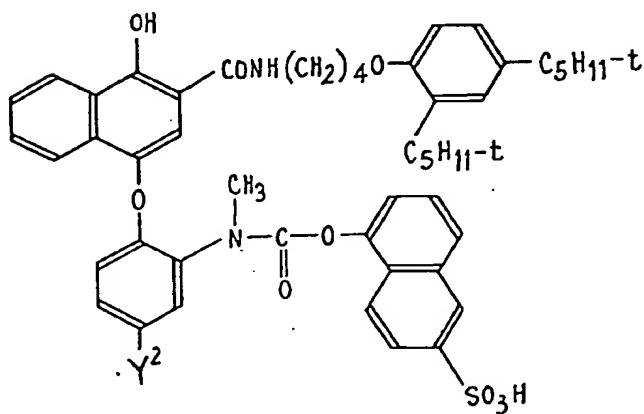
Coupler No.

 X^4

31

5-SO₂NH₂

32

6-SO₃H

Coupler No.

 Y^2

33

-NHCOC₁₅H₃₁

34

-NHCOC₄H₉

60

Preparative Example 6—Preparation of a cyan coupler which releases a bleach inhibitor

Using a reaction procedure similar to that of preparative Example 1, Coupler 35 was prepared.

5



Step 1



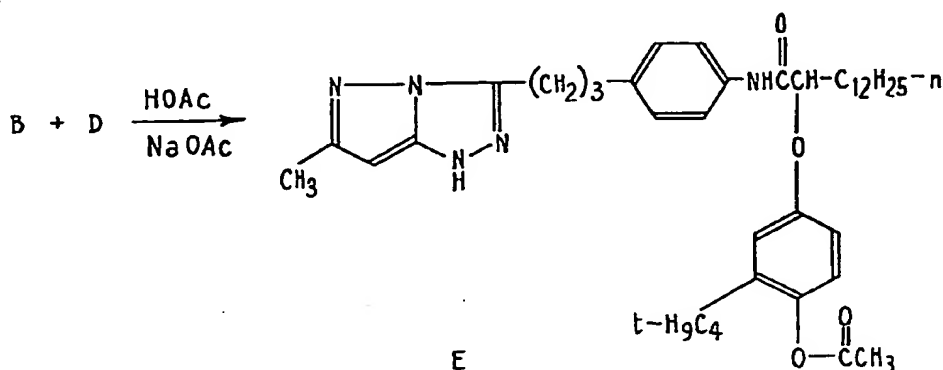
50

55



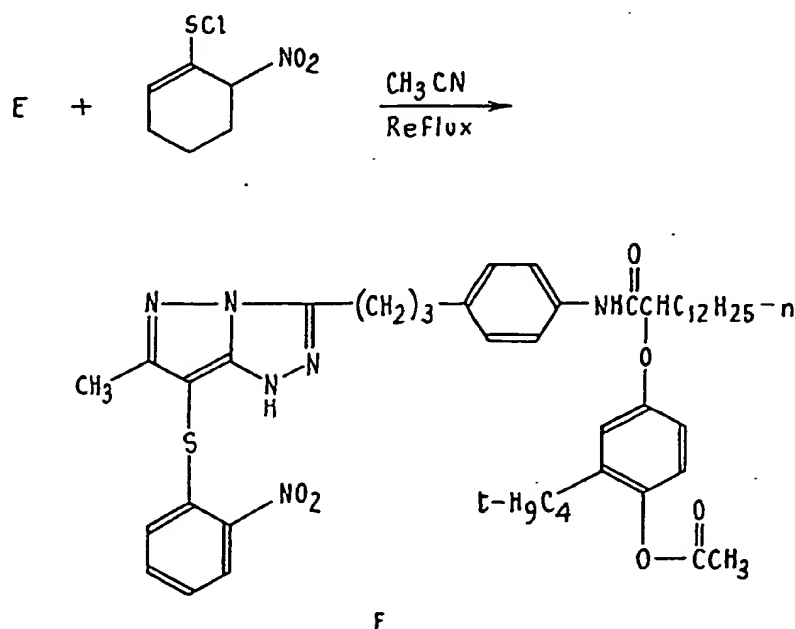
Compound C (150.0 g, 0.345 mole) was dissolved in 400 ml of thionyl chloride. Six drops of N,N-dimethylformamide (DMF) were added and the dark brown solution was refluxed for two hours. The excess thionyl chloride was removed by evaporation to give a dark brown oil. Toluene (100 ml) was added to the oil and the solution again evaporated to a dark brown oil. After vacuum drying overnight, the dark brown oil was taken up in 500 ml of ligroin, treated with charcoal, filtered, concentrated to 250 ml, and cooled in the refrigerator where the product crystallized as one solid mass. This was broken up and mixed with 150 ml of cold ligroin, chilled in a dry ice-acetone bath, filtered, washed with cold ligroin, recrystallized filtered, and vacuum dried to yield 132.3 g of white product, Compound D, m.p. 49.5, 50°C.

10 Step 3



Compound B (19.15 g, 0.075 mole) and sodium acetate (NaOAc) (6.15 g, 0.075 mole) were suspended in glacial acetic acid (HOAc) (200 ml) in a flask equipped with a calcium sulfate drying tube. After stirring for 15 minutes, a suspension of Compound D (33.98 g, 0.075 mole) in glacial acetic acid (50 ml) was added and the reaction mixture was stirred for two hours at room temperature. The reaction mixture was poured into two liters of ice water and the product was extracted with ethyl acetate. The organic extracts were washed repeatedly with water and 5% sodium bicarbonate solution, each containing sodium chloride. After drying over sodium sulphate, the extracts were concentrated to a brownish-yellow oil which was dissolved in a mixture of cyclohexane (230 ml) and ethyl acetate (10 ml), seeded, and allowed to stand for about 48 hours. The product crystallized in a solid mass. This was broken up, 500 ml hexane was added, and the fine solid was filtered, washed, air dried, and recrystallized to yield 26.4 g of off-white powdery solid, Compound E, m.p. 123–124°C.

Step 4



Compound E (33.6 g, 0.05 mole) and *o*-nitrobenzene-sulphenyl chloride (10.4 g, 0.055 mole) were mixed in dry acetonitrile (500 ml) and heated to reflux overnight, about 15 hours. The solvent was evaporated to give a reddish-brown gum which was partitioned between a mixture of ethyl acetate (250 ml), ether (150 ml) and aqueous 5% sodium bicarbonate solution. The organic phase was separated, washed twice with water (200 ml), dried over sodium sulphate, and concentrated to a reddish-brown foamy solid, which thin-layer chromatography showed to be pure. The material was recrystallized from ethyl acetate (50 ml) and hexane (250 ml) to yield 39.0 g yellow, crystalline solid, Compound F, m.p. 88.5–90°C.

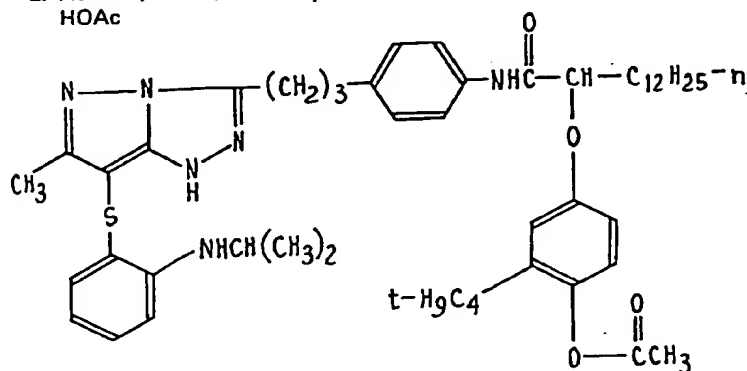
Step 5

10

F

1. H₂, 10% Pd/C
EtQAac

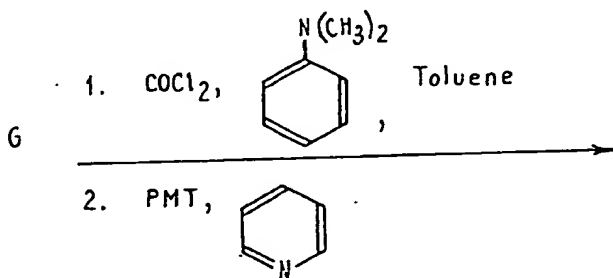
2. Acetone, TBAB,
HOAc

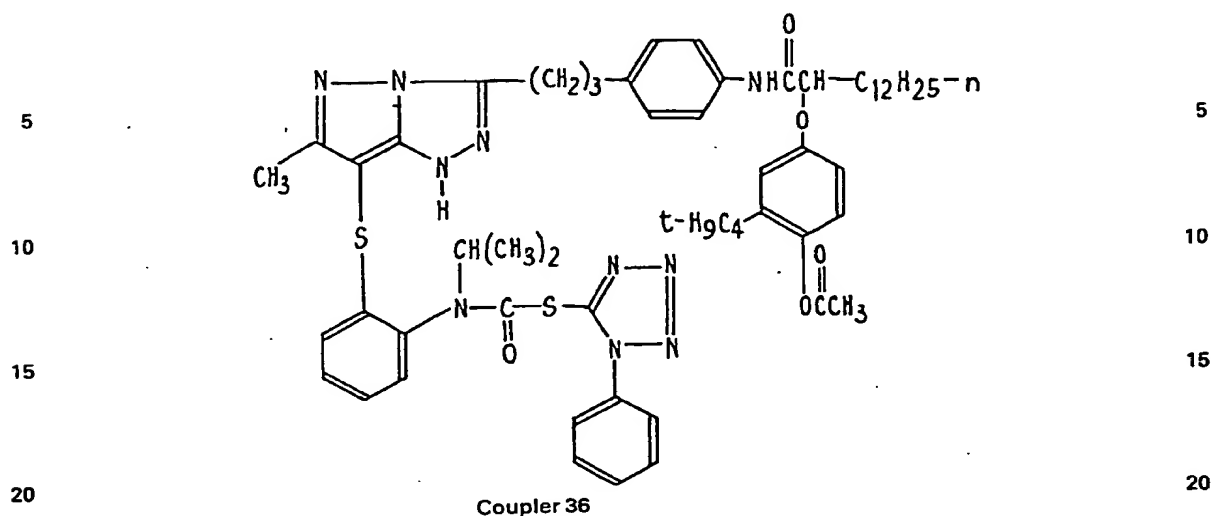


G

Compound F (16.5 g, 0.02 mole) 10% palladium on carbon (6 g), and ethyl acetate (250 ml) were mixed in a hydrogenation bottle and shaken 17 hours under hydrogen. Thin-layer chromatography indicated complete reaction. The catalyst was filtered off and the light yellow solution was evaporated to a pale yellow foamy solid which was vacuum dried for an hour. Acetone (11.6 g, 0.2 mole) and glacial acetic acid (80 ml) were added and the solution was cooled to about 15°C. After 15 minutes, a solution of *t*-butylamine borane (TBAB) (17.4 g, 0.2 mole) in acetic acid (70 ml) was added dropwise, with stirring, over a 20 minute period. After 3 hours, the reaction mixture was poured with stirring into one litre of ice water. The resultant white solid was collected, washed with water, and vacuum dried over phosphorous pentoxide to yield 14.3 g Compound G.

Step 6

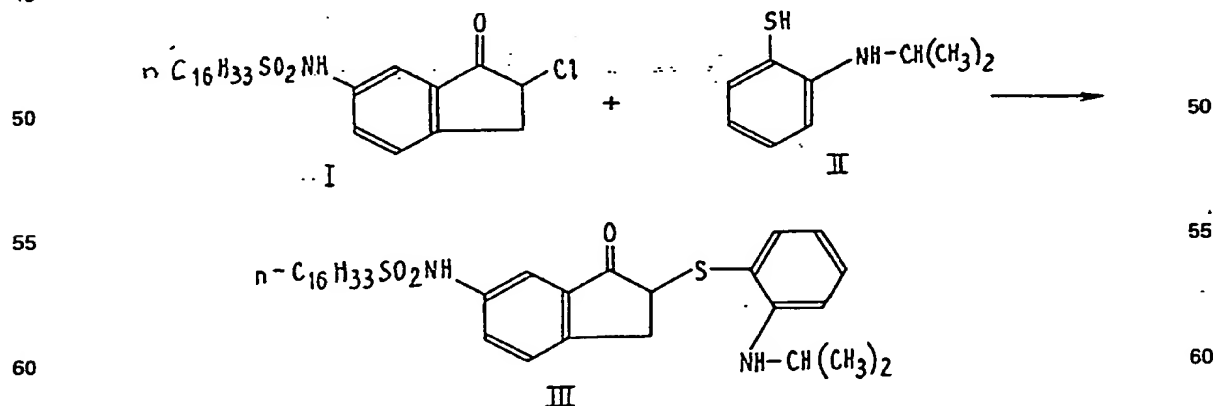




Compound G (4.18 g, 0.005 mole) was dissolved in toluene (50 ml), and the solution was cooled to about 0°C. With stirring, a solution of phosgene (12%) in toluene (4.12 g, 0.005 mole) was added dropwise over a 45 minute period. After 1 hour, thin-layer chromatography indicated that no reaction had occurred. N,N-Dimethylaniline (0.60 g, 0.005 mole) in 10 ml of toluene was added. After one hour, thin-layer chromatography indicated some reaction was occurring. Another two equivalents of N,N-dimethylaniline (1.20 g, 0.01 mole) were added dropwise, causing white solid to precipitate. More phosgene solution (4.12 g, 0.005 mole) was added and the reaction mixture was stirred at room temperature overnight (about 15 hours). Thin-layer chromatography indicated that little starting material remained. The toluene and excess phosgene were evaporated off and pyridine (75 ml) was added. To this was added dropwise, with stirring, 1-phenyl-2-mercapto-tetrazole (PMT) (0.89 g, 0.005 mole) in pyridine (30 ml). After stirring for five hours, the orangish reaction mixture was poured with stirring into 500 ml of ice water containing 150 ml of concentrated hydrochloric acid and extracted with methylene chloride. The extracts were washed with water and aqueous saturated sodium chloride solution, dried over sodium sulphate, filtered, and evaporated to yield 4.67 g of orange foamy solid. Elution with 10:1 methylene chloride-ethyl acetate from a column of silica gel isolated coupler 36 which was then confirmed by nuclear magnetic resonance spectroscopy and infrared spectroscopy. Anal. Calcd. for $C_{20}H_{12}N_4O_2S$: C, 65.7; H, 7.0; N, 13.4; S, 6.2. Found: C, 65.4; H, 5.7; N, 13.1; S, 5.9.

Preparative Example 8—Preparation of a coupler which yields a colorless reaction product and releases a development inhibitor

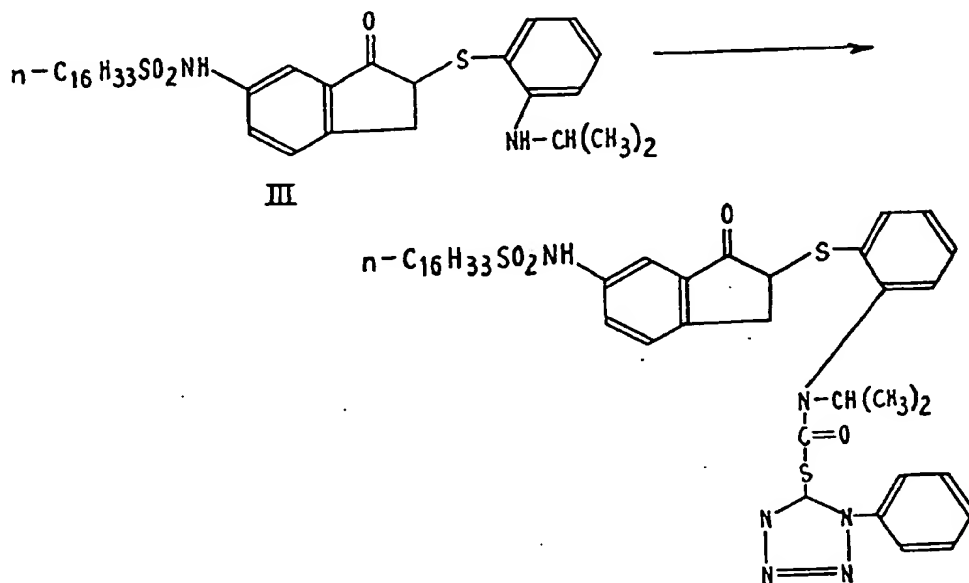
Step 1



To 8.2 g (0.02 mol.) of 2-chloro-6-hexadecylsulphon-amido indanone, suspended in 60 ml acetonitrile and 10 ml tetrahydrofuran, was added, at 0°C with stirring, a solution of 3.7 g (0.022 mol.) of 2-isopropylaminobenzenethiol in 10 ml of tetrahydrofuran and 2.8 g (0.022 mol.) of triethylamine. The mix-

ture was stirred for two hours and then poured into ice-water. The crude solid was collected, washed with water, and dried overnight.

Step 2



To 50 ml of toluene saturated with phosgene was added, with stirring at 0°C, a solution of 5.1 g (0.009 mol.) of 2-(2'-isopropylaminophenylthio)-6-hexadecylsulphonamido indanone (Compound III) in 50 ml toluene and 1.2 g (0.0095 mol.) of dimethylaniline. After stirring at 0-5°C for two hours, the solvent was removed under reduced pressure. The residue was dissolved in 50 ml pyridine, and 1.7 g of phenylmercaptotetrazole was added. The reaction mixture was stirred for four hours at 0-5°C and then poured into ice-water. The oil was extracted with ethyl acetate, dried over magnesium sulphate, and the solvent was removed to give a brown oil. The crude product was chromatographed through a silica gel column to yield 3 grams of Coupler 37.

Example 1 - Controlled Release of a Development Inhibitor

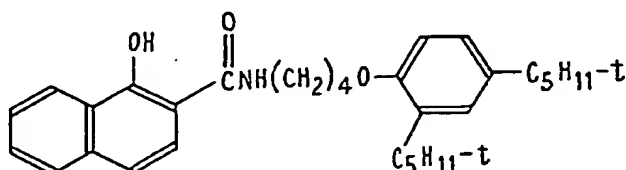
Four colour photographic elements illustrated by the following schematic structure were prepared. The numerical values denote coating coverages in g/m² unless otherwise indicated.

Gelatin - 0.86

AgX as Ag - 1.35; Cyan Dye Forming Coupler - 0.70; DIR Coupler - See below; Di-n-butyl phthalate - 0.5 g per g of total coupler, Gelatin - 2.7

//////////Film Support//////////

The cyan dye forming coupler has the formula:



Gelatin - 0.86

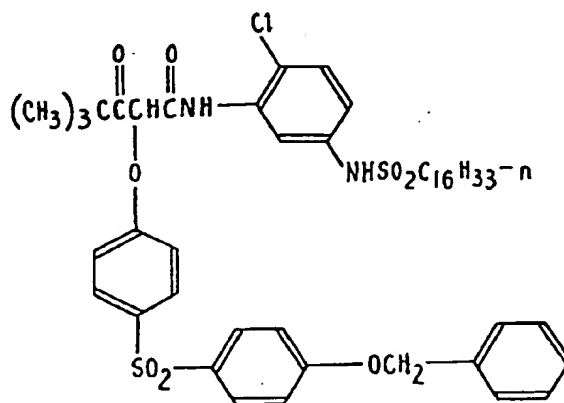
Green-sensitive AgBrI - 1.6; Gelatin - 2.41; Cyan dye-forming coupler - 0.47; DIR coupler - See below;
di-n-butyl phthalate - 0.5 g per g of total coupler

Antistain agent - 2,5-Didodecylhydro-quinone - 0.14; Gelatin - 0.58

Red-sensitive AgBrI - 1.6; Gelatin - 2.41; Yellow dye-forming coupler - 1.94 in Di-n-butyl phthalate - 0.97

//////////Film Support//////////

The cyan dye-forming coupler was the same coupler as employed in the materials of Example 1. The yellow dye-forming coupler was the structure:

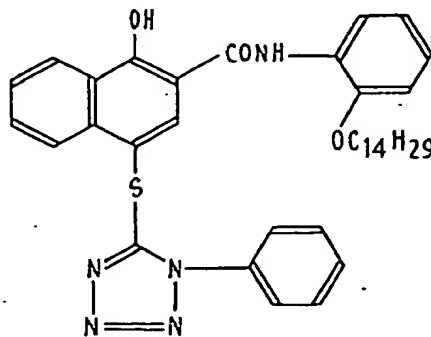


The materials contained development inhibitor releasing couplers as follows:

Material	DIR Coupler No.	g/m ²	mol/m ²
E	None	—	—
F	B	0.09	1.4×10^{-4}
G	3	0.31	3.5×10^{-4}
H	4	0.09	1.0×10^{-4}
I	5	0.29	3.3×10^{-4}

The amount of development inhibitor releasing coupler incorporated in each of the materials was chosen to provide cyan dye curves having essentially equal slopes.

Coupler B has the structure:



The five materials were exposed to green light through a graduated-density test object, then the test object was removed and the materials were uniformly flashed with red light. The materials were then colour developed for 2 minutes at 38°C using the composition described below, bleached, fixed and washed.

5	<i>Composition of Colour Developer Solution:</i>		5
	K ₂ SO ₃	2.0 g	
	4-Amino-3-methyl-N-ethyl-N-β-hydroxyethylamine sulphate	3.55 g	
10	K ₂ CO ₃ (anhydrous)	30.0 g	10
	KBr	1.25 g	
	KI	0.0006 g	
	Water to 1 litre		
15	pH to 11.0		15

During colour development oxidized colour developing agent generated in the green-sensitive layer (which has been stepwise exposed) couples with the cyan dye-forming coupler and the DIR coupler to form cyan dye and release directly (Coupler B) or indirectly (Couplers 3, 4 and 5) a development inhibitor. Oxidized colour developing agent generated in the red-sensitive layer (which has been uniformly exposed) couples with the yellow dye-forming coupler to form yellow dye. Development inhibitor released from the couplers migrates through the material until, in its active form, it inhibits silver halide development and affects the amount of dye formed in both of the layers. The effect on the red sensitive layer is proportional to the amount of development inhibitor released in the green-sensitive layer and depends upon the amount of active development inhibitor reaching it. These effects are measured by plotting the densities of cyan dye (in the green-sensitive layer) and yellow dye (in the red-sensitive layer). These plots are shown in Figures 2 to 6. It will be observed that in each of Material F to I, which contained development inhibitor releasing couplers, less yellow dye is formed in proportion to green exposure than in Material E which did not contain such a coupler; and that in Material G to I, which contained couplers of this invention, significantly less yellow dye is formed in proportion to green exposure than in Material F, which contained a prior art coupler. This indicates that a greater amount of active development inhibitor is reaching the red-sensitive layer when couplers of this invention are employed than reaches the red-sensitive layer when couplers of the prior art are employed and results in greater interimage effects.

35 *Example 3 – Release of a Yellow Image Dye*

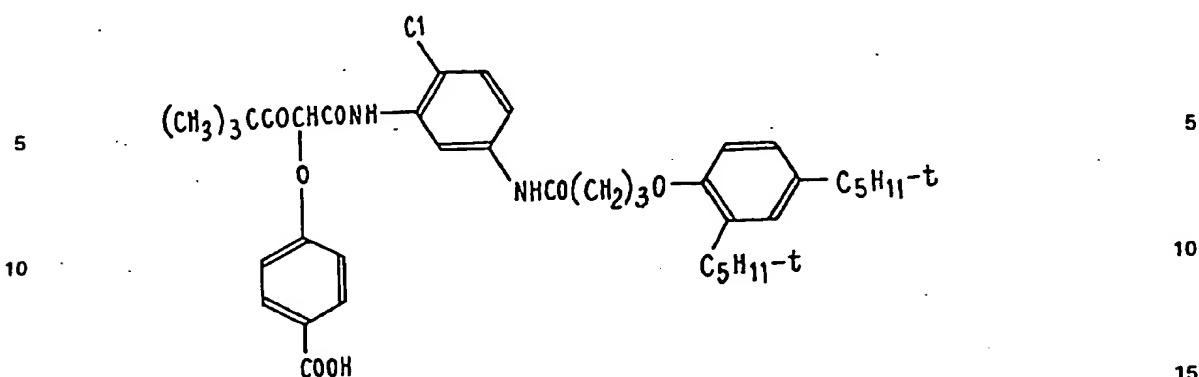
Three colour photographic materials illustrated by the following schematic structure were prepared. The numerical values denote coating coverages in g/m².

40	Gelatin – 0.54	40
	Gelatin – 2.70; AgX As Ag – 1.62; Yellow dye-forming coupler – See below; Di-n-butyl phthalate – 0.5 (g/g coupler)	

45 //////////////Film Support////////// 45

Material	Coupler	g/m ²	mol/m ²	
50 J (control)	C	1.3	0.0158	50
K (control)	C	0.65	0.0078	
55 L	26	0.65	0.0038	55

Coupler C has the structure:



The materials were exposed through a graduated-density test object, and processed at 38°C according to the following sequence:

Processing Sequence:

20	Colour Developer	2'
	4.3 g 4-Amino-3-methyl-N-ethyl-N-β-hydroxy-ethyl-aniline sulphate	
25	0.1 ml H_2SO_4	25
	2.0 g Sodium hexametaphosphate	
	4.0 g Na_2SO_3	
	20.0 g $Na_2CO_3 \cdot H_2O$	
	2.0 g KBr	30
30	Water to 1 litre, pH 11	
	Fix	2'
35	240 g $Na_2S_2O_3 \cdot 5H_2O$	35
	15 g Na_2SO_3	
	48 ml 28% Acetic Acid	
	7.5 g H_3BO_3	
	15 g Potassium Alum	
40	Water to 1 litre, pH 4.25	40
	Wash	2'
	Bleach	2'
45	21.5 g NaBr	45
	100.0 g $K_3Fe(CN)_6$	
	0.07 g $NaH_2PO_4 \cdot H_2O$	
	Water to 1 litre, pH to 7.0	
50	Wash	2'
	Fix	2'
	(same as above)	
55	Wash	2'
	Stabilizing Solution	2'
	5 g Cetyl trimethyl ammonium bromide	55
	20 g Na_2CO_3	
	Water to 1 litre, pH 11	
60	Wash	10'
		60

The resulting yellow dye images were evaluated by plotting yellow dye density vs. exposure. The results are shown in Figure 7. It will be observed that Material L, of the invention, yielded significantly more dye density than the materials containing prior art dyes, even though it contained less yellow coupler.

Example 4 - Release of a Cyan Image Dye

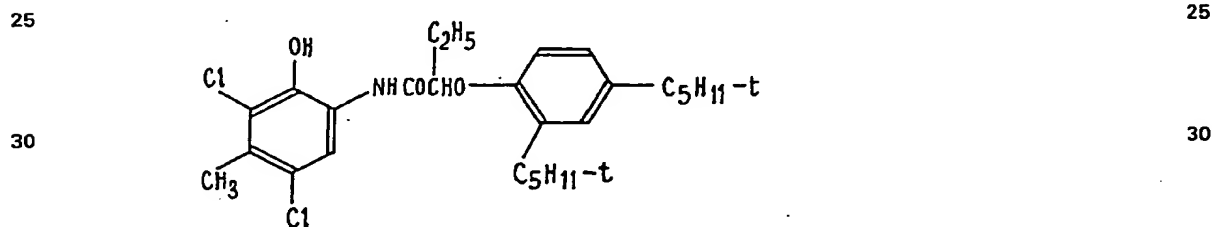
Three colour photographic materials illustrated by the following schematic structure were prepared. The numerical values denote coating coverages in g/m².

5	Gelatin - 0.54; Hardener - 0.081				5
	Red-sensitive AgX as Ag - 1.08; Cyan dye-forming coupler - See below; 2,4-di-n-amyphenol - 0.5 (g/g coupler);				
10	Gelatin - 2.70				10

//////////Film Support//////////

15	Material	Coupler	g/m ²	mol/m ²	15
	M	D	0.86	0.0149	
	N	D	0.43	0.0075	
20	O	23	1.40	0.0075	20

Coupler D has the structure:



35 The materials were exposed and processed as in Example 3, except that the development was for 20 minutes at 20°C in the following composition and that Materials M and N were not treated in the cetyl trimethyl ammonium bromide solution:

Composition of Colour Developing Solution:

40	Water			40
	K ₂ SO ₃	2.0	g	
	4-Amino-3-methyl-N-ethyl-N-β-(methane sulphonamide) ethyl-aniline			
45	sulphate hydrate	5.0	g	45
	Anhydrous K ₂ CO ₃	30	g	
	KBr	1.25	g	
	KI	0.0006	g	
50	Water to 1 litre pH to 11			50

The resulting cyan dye images were evaluated by plotting cyan dye density vs. exposure. The results 55 are shown in Figure 8. It will be observed that Material O, according to this invention, yielded substantially more dye than Material N, which contained an equimolar amount of a prior art coupler.

Example 5 - Release of a Competing Coupler

Three colour photographic materials illustrated by the following schematic structure were prepared. 60 The numerical values denote coating coverages in g/m².

41

Gelatin - 1.08

5

AgBrI emulsion - see below / Coupler -
see below / Tri-cresyl phosphate - 0.5
(g/g coupler); Gelatin 3.24

10

Antihalation layer

15

//////////Film Support//////////

20	Material	AgBrI as Ag	Cyan Dye-Forming Coupler	g/m ²	Coupler mols/m ²	20
	P control	1.08	D (See Ex 4)	0.26	0.052	
	Q	1.08	30	0.48	0.052	25
25	R	3.24	30	0.48	0.052	

30 Each material was exposed for 1/25 of a second through a neutral graduated-density test object and then processed at 38°C according to the following sequence.

Processing Sequence:

35	Colour developer	1'	35
	2.0 g K ₂ SO ₃		
	2.45 g 4-Amino-3-methyl-N,N-diethyl-aniline hydrochloride		
	30.0 g K ₂ CO ₃ (anhydrous)		
	1.25 g RBr		
40	0.0006 g KI		40
	Water to 1 litre		
	pH to 10.0		
	10% Acetic Acid Stop	4'	45
45	Bleach	4'	
	175 ml 1.56 Molar Ammonium Ferric Ethylenediamine tetraacetic acid		
	150 g NH ₄ Br		
50	10.5 ml Acetic Acid		50
	35 g NaNO ₃		
	Water to 1 litre		
	Wash	3'	55
55	Fix	4'	
	162 ml 60% Ammonium thiosulphate solution		
	13 g Sodium Hydrogen Sulphite		
60	2.83 ml 50% NaOH Solution		60
	Water to 1 litre		
	Wash	3'	
65	Stabilizer	1'	65

10.0 ml 10% Wetting Agent
6.0 ml 35% Formalin
..... Water to 1 litre

5 The resulting cyan dye images were evaluated by plotting cyan dye density vs exposure. The results are shown in Figure 9. It will be observed that for equivalent amounts of silver (Materials P and Q) less dye density was obtained with a coupler of this invention than with a prior art coupler. In order to obtain equivalent density with a coupler of this invention approximately three times as much silver halide was required (Material R). Both of these observations indicate that competing coupler was being released and 10 was competing for oxidized colour developing agent with the cyan dye forming coupler.

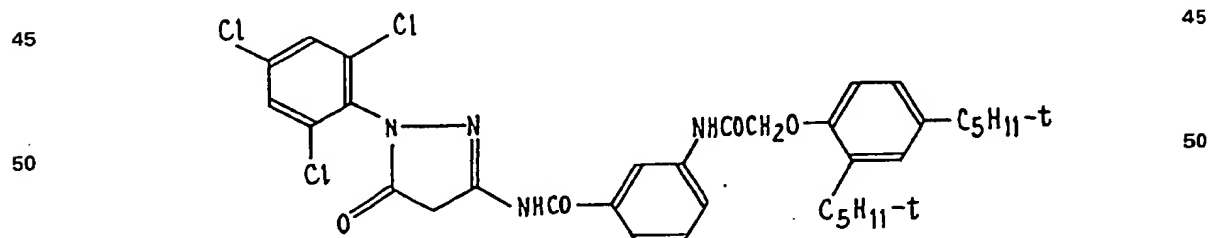
Example 6 - Interimage Effects

Two multilayer colour negative film materials identified by the following schematic structure were prepared. The numerical values denote coating coverages in g/m².

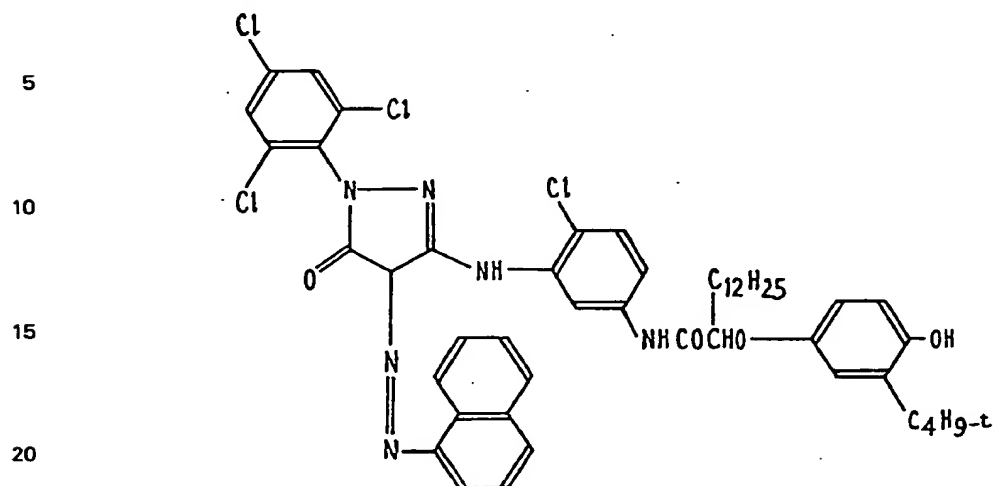
15		15
	Gelatin Overcoat	
20		20
	Ultraviolet Protective Overcoat	
25		25
	Fast blue-sensitive, yellow-dye-forming silver halide emulsion layer;	
	Blue-sensitive AgX as Ag - 0.93	
	Yellow coupler (see Example 2) - 0.30 in di-n-butyl	
30	phthalate - 0.10;	30
	Gelatin - 0.61	
35		35
	Slow blue-sensitive, yellow dye-forming silver halide emulsion layer;	
	Blue-sensitive AgX as Ag - 0.62;	
	Yellow Coupler (see Example 2) - 1.25 in di-n-butyl	
	phthalate - 0.42;	
40	Gelatin - 1.99	40
45		45
	Yellow Colloidal Silver Filter Layer	
50		50
	Fast green-sensitive magenta-dye-forming silver halide emulsion layer;	
	Green-sensitive AgX as Ag - 1.23;	
	Magenta Coupler (see below) - 0.098 in tricresyl phosphate - 0.098;	
	Coloured magenta coupler (see below) - 0.03 in tricresyl phosphate - 0.03;	
55	Gelatin - 0.63	55

5	Slow green-sensitive magenta-dye-forming silver halide emulsion layer; Green-sensitive AgX as Ag - 1.49; Magenta coupler (see below) - 0.59 in tricresyl phosphate - 0.59; Coloured magenta coupler (see below) - 0.092 in tricresyl phosphate 0.92; Magenta DIR coupler (see below) - 0.019 in tricresyl phosphate - 0.039; Gelatin - 1.25	5
10		10
15	Gelatin Interlayer	15
20	Fast red-sensitive cyan-dye-forming silver halide emulsion layer; Red-sensitive AgX as Ag - 1.31; Cyan coupler (see Example 1) - 0.97 in di-n-butyl phthalate - 0.48; Coloured cyan coupler (see below) - 0.004 in tri-n-butyl phthalate - 0.002; Gelatin - 0.61	20
25		25
30	Slow red-sensitive cyan-dye-forming silver halide emulsion layer; Red-sensitive AgX as Ag - 2.26; Cyan coupler (see Example 1) - 0.59 in di-n-butyl phthalate - 0.29; Coloured cyan coupler (see below) - 0.053 in di-n-butyl phthalate - 0.027; DIR coupler (see below); Gelatin - (see below)	30
35		35
40	Antihalation Layer	40
45	//////////Film Support//////////	45

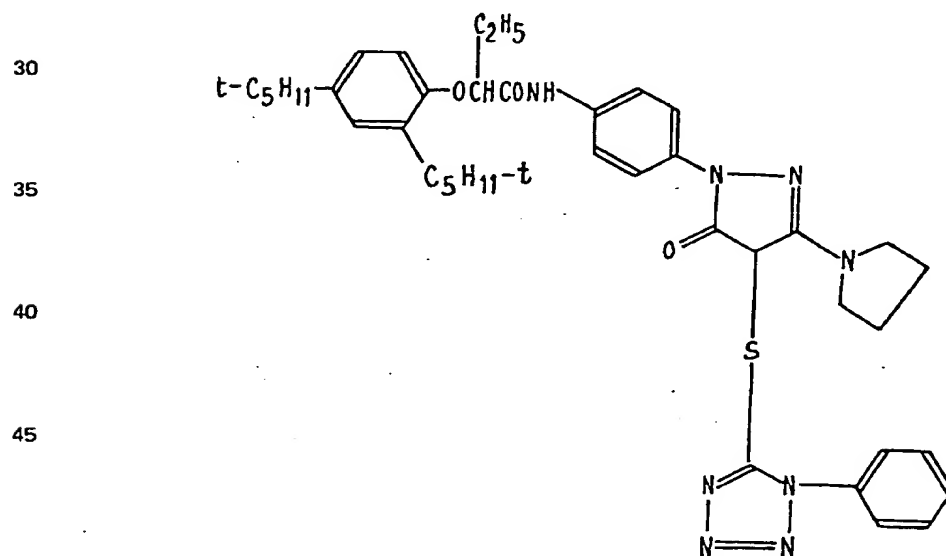
The magenta coupler has the structure



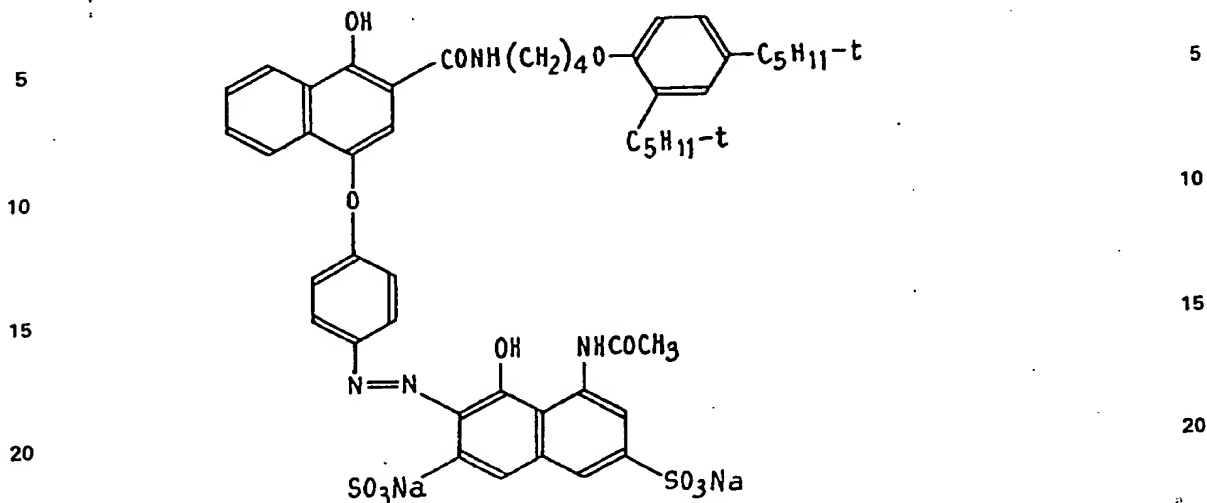
The coloured magenta coupler has the structure



25 The magenta DIR coupler has the structure



The coloured cyan coupler has the structure



The materials also contained in the slow red sensitive layer DIR coupler as follows. The amount of coupler was such as to provide similar D vs. Log E curves.

Material	Coupler (g/m ²)	Gelatin (g/m ²)
S	B (See Ex. 2) — 0.029 in diethyl lauramide — 0.058	1.74
T	4 — 0.072 in N-n-Butylacetanilide — 0.14	2.08

Each material was exposed for 1/4 second, through a sinusoidal test pattern with a special frequency range of 2.5–100 cycles/mm, with a tungsten illuminant filter to a colour temperature of approximately 40 6500°K, colour developed for 3 1/4 minutes at 38°C in the composition shown in Example 1, bleached, fixed and washed.

The modulation transfer functions of the processed material were then determined by the procedure described in the American National Standard Method for determining the Photographic Modulation Transfer Function of Photographic Films, PH 2-337, January, 1973.

It was observed that Material T (the invention) had improved cyan and magenta modulation transfer functions in the spatial frequency range of 10–40 cycles/mm, compared with Material S (control). Thus, the couplers of this invention can provide multilayer materials of improved sharpness. For example, at 20 cycles/mm, in Material T, the percent response of the cyan layer was about 108 and the percent response of the magenta layer was about 112, while in Material S the comparable values were 90 and 100 percent.

Example 7

Photographic material similar to those of Example 2 were prepared having the following schematic structure:

Gelatin	
Green-sensitive AgX gelatino emulsion layer containing a DIR coupler in 2 parts by weight of diethyl lauramide and a cyan-dye-forming coupler or a magenta-dye-forming coupler in 1/2 part by weight of di-n-butyl phthalate	

Interlayer

- 5 Red-sensitive AgX gelatino emulsion layer containing a yellow dye forming coupler in 1/2 part by weight of d-n-butyl phthalate

5

10 Film Support

10

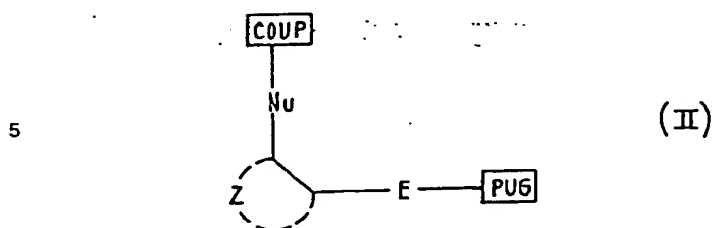
The amount of DIR coupler in the green-sensitive layer was adjusted so that when that layer was stepwise exposed and processed, as described below the density vs. log exposure plot had a slope (γ) of about 0.65. The following couplers, shown in the preparative examples were compared with analogous prior art couplers: Couplers 7, 13, 14, 18, 19 and 36. The materials were given a stepwise minus blue exposure, (using a Wratten 12 filter) colour developed in the composition shown in Example 2 (but adjusted to pH 10) for 2 1/4 minutes at 38°C., fixed, bleached, fixed and washed. For each of the materials there was plotted the density, as a function of log exposure, of the red-sensitive layer (which contains yellow dye) to blue light and the density of the green-sensitive layer to red or green light (depending upon whether the dye-forming coupler yielded a cyan or magenta dye). The slope (γ) of the resultant curves was measured and the ratio between the slope of the curve for the green-sensitive layer and the slope of the curve for the red-sensitive layer (γ_G/γ_R) was calculated. This ratio is a measure of the interlayer interimage effect on the red-sensitive layer of development inhibitor released in the green-sensitive layer. Inasmuch as development inhibitor reaching the red-sensitive layer would reduce the slope of the density vs. log exposure curve for that layer, the greater the ratio γ_G/γ_R , the greater the interimage effect. It was observed that with the couplers of this invention the ratio γ_G/γ_R was greater than that with analogous prior art couplers, and thus, the present couplers provided a greater interimage effect than the analogous prior art couplers.

The material were exposed to green light through a sinusoidal test pattern, as described in Example 6, processed as described above and modulation transfer function curves for the green sensitive layer were obtained as described in Example 6. From these curves it was observed that couplers of the present invention provided sharper images than analogous couplers of the prior art.

35 CLAIMS

35

1. A photographic material comprising a support, at least one photosensitive silver halide emulsion layer and associated therewith a photographic coupler comprising a coupler group and a releasable photographically useful group, characterized in that the coupler contains a timing group, joining said coupler and photographically useful groups, which is cleavable from said coupler group on reaction with oxidized colour developing agent and the resulting cleaved timing and photographically useful group entity is able to undergo an intramolecular nucleophilic displacement reaction to make available a photographically useful compound.
2. A photographic material as claimed in Claim 1 in which the timing group comprises:
 - (A) a nucleophilic group attached to the coupler group at a position from which it is displaced by oxidized colour developing agent,
 - (B) an electrophilic group attached to the photographically useful group, and
 - (C) a linking group spatially relating said groups (A) and (B) so that after cleavage of (A) from the coupler group, they are able to undergo an intramolecular nucleophilic displacement reaction cleaving the photographically useful group from the timing group.
3. A photographic material as claimed in Claim 2 in which the linking group (C) is such that the nucleophilic displacement reaction leads to the formation of a 3- to 7- membered ring.
4. A photographic material as claimed in any of Claims 1-3 in which the nucleophilic group contains an electron rich oxygen, sulphur or nitrogen atom.
5. A photographic material as claimed in any of Claims 1-4 in which the electrophilic group contains an electron deficient carbonyl, thiocarbonyl, phosphinyl or thiophosphinyl group.
6. A photographic material as claimed in any of Claims 1-5 in which the photographic coupler has the formula:



10 wherein

COUP is a coupler group,

Nu is a nucleophilic group, attached to the coupling position of COUP, of the formula $-O-CR_2$, $-O-CO-$, $-NR-CO$, $-O-$, $-S-$, $-S-CR_2$ or $-NR-SO_2-$ in which the left hand end is attached to COUP,

Z represents the atoms necessary to complete a mono- or bicyclic aromatic or heterocyclic ring system containing 5 to 10 ring atoms which may be substituted,

E is an electrophilic group of the formula $-(CR_2)_n-CO-$, $-(CR_2)_n-NR-CO-$ or $-(CR_2)_n-CS-$ or $-(CR_2)_n-NR-CS-$ in which the right hand is attached to PUG,

PUG is a photographically useful group,

n is 0, 1, 2, 3 or 4 such that on completion of the nucleophilic displacement reaction a ring having 5 or 6 ring members is formed, and each R is independently, hydrogen or an alkyl group of 1-20 carbon atoms.

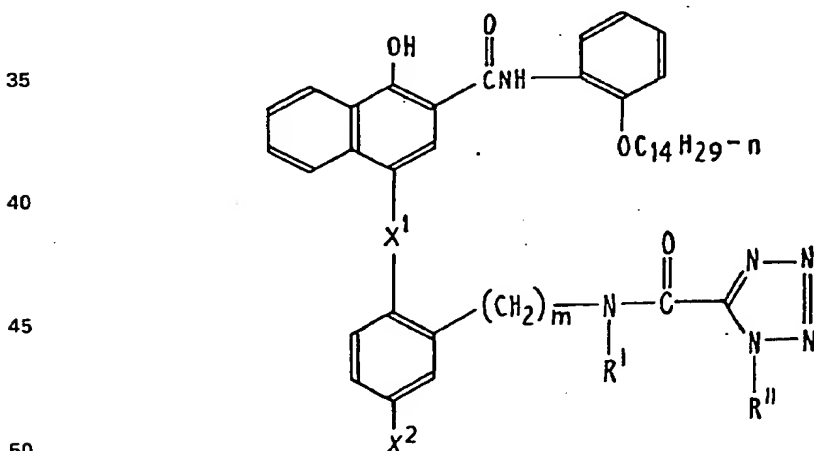
7. A photographic material as claimed in any of Claims 1-6 in which the photographically useful group contains a hetero atom from Group VA or Group VIA of the periodic table identified hereinbefore having a negative valence of 2 or 3 which is attached to the electrophilic group.

8. A photographic material as claimed in Claim 7 in which the hetero atom is oxygen, sulphur or nitrogen.

9. A photographic material as claimed in any of Claims 1-8 in which the photographically useful group is the radical of a development inhibitor, dye, dye precursor, coupler, developing agent or bleach inhibitor.

10. A photographic material as claimed in Claim 9 in which the photographically useful group is the radical of a mercapto-tetrazole or benzotriazole developing inhibitor.

11. A photographic material as claimed in Claim 1 in which the photographic coupler has the formula.



where:

X¹ is oxygen or sulphur;

X² is hydrogen, nitro, alkoxy-carbonyl or alkyl-sulphonamido,

m is 0 or 1,

R¹ is alkyl of 1-4 carbon atoms, and

R² is phenyl or alkyl of 1-4 carbon atoms.

12. A photographic material according to Claim 1 substantially as described herein and with reference to Examples 1-7.

13. A photographic coupler as defined in any of Claims 1-11.

14. A photographic coupler according to Claim 13 substantially as defined herein and with reference to Preparative Examples 1-8.

15. A method of forming a photographic image which includes the step of developing an imagewise exposed silver halide emulsion layer with a colour developing agent in the presence of a coupler according to Claim 13 or 14.

16. A method as claimed in Claim 15 in which the coupler is contained in the processing solution containing the colour developing agent.

17. A method as claimed in Claim 15 in which the coupler is incorporated in or adjacent the silver halide emulsion layer.

5 18. A method according to Claim 15 substantially as described herein and with reference to Examples 1-7

5